

## Simplifying Chemical Kinetics: Intrinsic Low-Dimensional Manifolds in Composition Space

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A general procedure for simplifying chemical kinetics is developed, based on the dynamical systems approach. In contrast to conventional reduced mechanisms no information is required concerning which reactions are to be assumed to be in partial equilibrium nor which species are assumed to be in steady state. The only "inputs" to the procedure are the detailed kinetics mechanism and the number of degrees of freedom required in the simplified scheme. (Four degrees of freedom corresponds to a four-step mechanism, etc.) The state properties given by the simplified scheme are automatically determined as functions of the coordinates associated with the degrees of freedom. Results are presented for the CO/H<sub>2</sub>/air system. These show that the method provides accurate results even in regimes (e.g., at low temperatures) where conventional mechanisms fail.

### INTRODUCTION

In the last two decades a triumph of combustion research has been the detailed computation of one-dimensional laminar flames [1-3]. The agreement between measurements and these calculations demonstrates that we have adequate knowledge of the reaction and transport mechanisms (at least for simple fuels). A typical reaction mechanism (for methane, say) involves about 40 species and 200 reactions.

For more general flows, the numerical solution of the conservation equations including detailed kinetics is computationally demanding, or even prohibitive. For example, Smooke et al. [4] report that 150 h of supercomputer time were required to make calculations of a steady, axisymmetric, methane-air diffusion flame. Thus it is highly desirable to develop methods that make mathematical simplifications to the reaction kinetics, without sacrificing accuracy.

Simplified kinetic schemes are in particular demand for making turbulent combustion calculations. The recent works of Chen et al. [5] well illustrate current approaches. Simplified three- or four-step schemes have been developed by sev-

eral groups (e.g., Peters and Kee [6], Bilger and Kee [7], Chen [8]). These schemes represent the thermodynamical state of the fluid in terms of four or five variables (rather than more than 40 required by the detailed mechanism). The state properties can then be tabulated as functions of these four or five variables, and these tables are used in the turbulent-combustion calculation.

Current approaches to devising reduced mechanisms are described by Smooke [9]. Principal ingredients are partial equilibrium and steady-state assumptions for particular reactions and species. This type of approach has three drawbacks:

1. For each fuel/oxidizer system, and for each order of the scheme (i.e., two-step, four-step, etc.) considerable human time and labor is required to develop the method.
2. The partial-equilibrium and steady-state assumptions invoked are inevitably applied to ranges of compositions and temperatures where they provide poor approximations.
3. Error estimates or limits of applicability are only obtained by comparison of results obtained both by a detailed and the reduced reaction mechanism, but not from the method itself.

We develop here a general procedure for simplifying chemical kinetics which is free of these

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drawbacks. The “inputs” to the procedure are the detailed kinetics mechanism and the number of degrees of freedom required in the simplified scheme. (Four degrees of freedom corresponds to a four-step mechanism, etc.) No information is required concerning which reactions are to be assumed to be in partial equilibrium.

The mathematical model for gas-phase chemical reaction systems consists of a set of partial differential equations, namely the conservation equations, which describe the time-dependent development of all the properties that determine the state of the system (e.g., species mass fractions, specific enthalpy, pressure and velocity field). The governing processes (i.e., flow, molecular transport, and chemical reaction) occur at time scales that differ by orders of magnitude. Chemical reaction usually is governed (e.g., in combustion processes) by time scales ranging from  $10^{-9}$  to  $10^2$  s. If we look at a typical spectrum of time scales as it occurs, for example, in flames (presented schematically in Fig. 1), it can be seen that the chemical time scales cover a larger range than the so-called physical time scales (denoting, e.g., molecular transport). The very fast time scales in chemical kinetics are usually responsible for equilibration processes (reactions are in partial equilibrium, species are in steady state). If we make use of the fact that those time scales are very fast, it is possible to decouple them, that is, we can assume local equilibrium with respect to the fastest time scales.

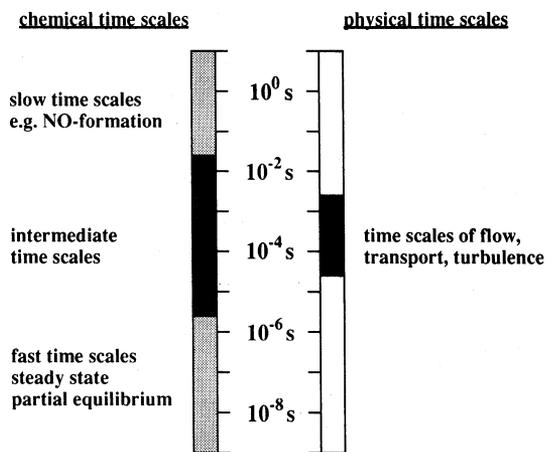


Fig. 1. Schematic illustration of the time scales governing a chemically reacting flow.

For the simplest case (homogeneous, adiabatic isobaric reaction) the state of the reacting system is described by a set of  $n_s$  ordinary differential equations, where  $n_s$  is the number of species involved in the detailed kinetics scheme. Thus  $n_s$  different time scales govern the process and  $n_s$  variables are needed in order to describe the system. The advantage of decoupling the fast time scales is the following: if we decouple, say, the  $n_f$  fastest time scales, the remaining number of time scales is given by  $n_g = n_s - n_f$ , and the system can be described in terms of a much smaller number (i.e.,  $n_g$ ) of variables (degrees of freedom). In addition to reducing the number of equations that have to be solved in complex flow problems, there is one major advantage of this reduction of the number of state variables: very often (e.g., in pdf methods for turbulent flows) the computation of the chemical rates of change is so time consuming that it is desirable not to calculate them directly, but to use a table lookup. For combustion processes, which are governed by a large number of different species and reactions, a table setup for a detailed reaction mechanism would be impossible (a methane-air flame would already need a more than 30-dimensional table, exceeding any available storage on a computer). But if we are able to describe the chemical system in terms of a small number (say, e.g., five) variables, such a table setup is practicable.

In this work we develop a method that allows decoupling the fast time scales of chemical reactions and thus globally reduces the dimension of the composition space of the chemical system. Based on an eigenvector analysis of the governing equations in a homogeneous chemical reaction system, the local time scales in the composition space (which are associated with the eigenvalues) are identified and the state properties given by the simplified scheme are automatically determined as functions of the coordinates associated with the degrees of freedom.

Existing simplified schemes involve partial-equilibrium and steady-state assumptions. The imposition of  $n_f$  ( $n_f < n_r$ ) such assumptions defines an  $n_g$ -dimensional manifold ( $n_g = n_s - n_f$ ) to which (by assumption) the state is confined. The reduced  $n_g$ -step scheme yields trajectories on this manifold. Different imposed assumptions yield different manifolds. The method developed

here defines an intrinsic  $n_g$ -dimensional manifold: the  $n_f$  local conditions that generate the manifold stem from the eigenvalue–eigenvector representation of the local Jacobian matrix. This intrinsic manifold is optimal in at least two respects. First, for initial conditions on the manifold, the trajectories are exact for linear systems (i.e., the detailed and reduced schemes are identical). Second, for initial conditions off the manifold, the resulting trajectories are optimally attracted to the manifold.

The concepts we use are those used in the study of dynamical systems. Herein we agree with the approach of Lam and Goussis [11–13], who use the dynamical systems approach in order to simplify chemical kinetics. Using a CSP (computational singular perturbation) method, they identify the available simplifications of the chemical kinetics of a given reaction system, decouple the fastest time scales, and thus are able to remove the stiffness of the ordinary differential equation system and solve it by explicit methods obtaining a high accuracy. Although using similar methods, our approach is different. We use the dynamical system approach, not in order to overcome the stiffness of the differential equation system, but in order to develop a scheme that reduces the state space of a reaction system globally in such a way that it can be tabulated for subsequent use in turbulent combustion calculations (e.g., in pdf methods [14, 15]).

In the next sections, the problem is formulated mathematically. Results are then given for the CO/H<sub>2</sub>/air system. These confirm the favorable properties claimed above. While the development is mathematical, no attempt at rigor is made. In particular, the existence, uniqueness, and smoothness of several manifolds is implicitly assumed without comment.

## GEOMETRICAL REPRESENTATION OF CHEMICAL KINETICS

### General Reactive System

The mathematical model for gas-phase chemical reaction systems consists of a set of partial-differential equations, namely the conservation equations, which describes the time-dependent development of all the properties that determine

the state of the system (e.g., species mass fractions  $w_i$ , specific enthalpy  $h$ , density  $\rho$ , and velocity field  $v$ ) [16, 17]. In its most general form, this equation system can be written as

$$\frac{\partial \rho}{\partial t} = \tilde{\Gamma}_\rho, \quad (1)$$

$$\frac{\partial \rho v}{\partial t} = \tilde{\Gamma}_v, \quad (2)$$

$$\frac{\partial \rho w_i}{\partial t} = \tilde{\Gamma}_{w_i} + \tilde{\Omega}_i, \quad (3)$$

$$\frac{\partial \rho h}{\partial t} = \tilde{\Gamma}_h, \quad (4)$$

together with equations of state

$$P = \hat{P}(\rho, h, \mathbf{w}), \quad (5)$$

$$T = \hat{T}(\rho, h, \mathbf{w}), \quad (6)$$

where  $P$  is the pressure and  $T$  is the temperature. The terms  $\Gamma$  denote expressions that account for convection, molecular transport, external forces, etc. Chemical reaction is introduced only by a source term  $\tilde{\Omega}_i$  in the species equations because it creates neither mass, momentum, nor energy. Although very simple in appearance, this equation system can be very difficult to solve, especially if space-dependent problems are treated (see, e.g., Ref. 18).

### Simple Homogeneous System

Although we are interested in the general case formulated above, the development of the method is performed for the simplest case of a spatially homogeneous, adiabatic, isobaric system. In this case the whole equation system simplifies to

$$\frac{\partial h}{\partial t} = 0, \quad (7)$$

$$\frac{\partial P}{\partial t} = 0, \quad (8)$$

$$\frac{\partial \phi_i}{\partial t} = \Omega_i, \quad (9)$$

where the term for chemical reaction is given by

$$\Omega_i = \frac{\dot{\omega}_i(h, P, \phi)}{\rho(h, P, \phi)}. \quad (10)$$

In these equations  $\dot{\omega}_i$  denotes the molar rate of production of a chemical species  $i$  due to chemical reaction, and  $\phi_i$  is its *specific mole number*, which is defined by:  $\phi_i = w_i/M_i$ , where  $M_i$  is the molar mass of species  $i$ . This nomenclature is chosen because  $\phi_i$  also can be regarded as the number of moles of species  $i$  per unit mass. In the discussion section we return to the general case and discuss the influences of  $\Gamma_h$ ,  $\Gamma_P$ , and  $\Gamma_{\phi_i}$  that are absent from Eqs. 7-9.

### State, Composition and Reaction Spaces

At any time  $t$ , the simple homogeneous system considered is completely determined by a set of state variables, namely the total enthalpy, the pressure, and  $n_s$  composition variables (with  $n_s$  as the number of species in the reaction system). Thus the state of the system at any time can be represented as a point in a  $(2 + n_s)$ -dimensional state space  $\Sigma$ , and the solution of Eqs. 7-9 describes the trajectory of the system in this space.

Since the system considered is adiabatic and isobaric,  $h$  and  $P$  are fixed in time (see Eqs. 7 and 8). Consequently it is sufficient to consider the  $n_s$ -dimensional composition space  $\Phi$ . It is useful to regard  $\Phi$  as a vector space, and hence at any time  $t$ , the composition is a vector  $\phi(t)$  in this space. In the natural basis, the coordinates of the vector are  $\phi = (\phi_1, \phi_2, \dots, \phi_{n_s})^T$ .

Above it was pointed out that there are two state variables that do not change with time ( $h$  and  $P$ ). By the law of element conservation there are  $n_e$  (= number of different elements in the reaction system) additional variables that do not change with time, namely the *specific element mole numbers*  $\chi_i$ , which are defined by  $\chi_i = z_i/\bar{M}_i$ , where  $z_i$  is the element mass fraction and  $\bar{M}_i$  the molar mass of the element  $i$ .

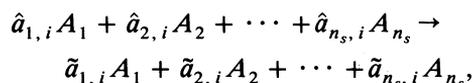
Let  $\mu_{j,i}$  denote the number of atoms of element  $i$  in a species  $j$ . Then  $\mu_i = (\mu_{1,i}, \mu_{2,i}, \dots, \mu_{n_s,i})^T$  shall be called the *element composition vectors*. The specific element mole numbers result from the specific mole numbers according to

$$\chi_i = \sum_{n_s} \mu_{k,i} \phi_k = \mu_i^T \phi. \quad (11)$$

It can be shown that the  $\chi_i$  do not change with

time.

For each element there is a corresponding element vector  $\mu_i$ . Similarly, we have a *reaction vector*  $\nu_i$  for each elementary chemical reaction [11]. With  $A_k$  denoting a molecule of species  $k$ , the  $i$ th reaction can be written as



where  $\hat{a}_{k,i}$  and  $\tilde{a}_{k,i}$  are integers defining the reaction. With the stoichiometric coefficients being  $\nu_{k,i} = \tilde{a}_{k,i} - \hat{a}_{k,i}$ , the reaction vector for reaction  $i$  is defined by  $\nu_i = (\nu_{1,i}, \nu_{2,i}, \dots, \nu_{n_s,i})^T$ . Element conservation in chemical reactions forces

$$\sum_{k=1}^{n_s} \nu_{k,i} \mu_{k,j} = 0 \quad \text{or} \quad \nu_i^T \mu_j = 0 \quad (12)$$

for all reactions  $i$  and elements  $j$ . Thus all element vectors are orthogonal to all reaction vectors. The way of looking at a chemical reaction system in terms of element and reaction vectors may seem a little strange at first, but it provides a useful tool for theoretical investigations.

We define the *reaction subspace*  $R$  to be the space spanned by the reaction vectors  $\nu_i$ . The dimensionality of this space is  $n_r = n_s - n_e$ . This is the case provided there are no inert species. If there are inert species, these can be treated as additional "elements," with corresponding element vectors  $\mu_i$ , and corresponding (fixed)  $\chi_i$ . It follows that the  $n_e$  element vectors  $\mu_i$  and any  $n_r$  linearly independent reaction vectors  $\nu_i$  span the composition space  $\Phi$ . Consequently such a set of vectors can be used as an alternative basis for  $\Phi$ .

Finally we note, that not every point in  $\Phi$  (or  $\Sigma$ ) corresponds to a realizable composition (or state). Rather there is a realizable region given by the conditions

$$T(h, P, \phi) > 0 \quad (\text{boundedness of temperature}), \quad (13)$$

$$P > 0 \quad (\text{boundedness of pressure}), \quad (14)$$

$$0 \leq M_i \phi_i \leq 1 \quad (\text{boundedness of mass fractions}), \quad (15)$$

$$\sum_{i=1}^{n_s} w_i = \sum_{i=1}^{n_s} M_i \phi_i = \sum_{i=1}^{n_e} \bar{M}_i \chi_i = 1 \quad (\text{normalization}). \quad (16)$$

Equation 16 gives three equivalent statements of the constraint that mass fractions sum to unity. This last constraint is different from the others, because it not only limits the space, but actually reduces the dimension of the accessible space by one. That is, in the  $n_s$ -dimensional composition space  $\Phi$ , realizable compositions are restricted to the  $(n_s - 1)$  dimensional linear manifold  $M$ , for which Eq. 16 is satisfied.

Equation 15 (by itself) restricts realizable compositions to a simplex  $S_\Phi$  in  $\Phi$ . Thus, in combination, Eqs. 15 and 16 confine realizable compositions to the intersection of  $M$  and  $S_\Phi$ , which is a  $(n_s - 1)$ -dimensional simplex, whose boundary is denoted by  $\partial\Phi$ .

This rather formal way of looking at chemical kinetics can be illustrated by a simple example, such as the  $O_3/O_2/O$  system. In this case we have a three-dimensional composition space, the composition being given by  $\phi = (\phi_{O_3}, \phi_{O_2}, \phi_O)$ . Due to element conservation (in this case, because we have only one element, equivalent to the law of mass fractions summing to 1), possible states of the chemical system are confined to a plane defined by

$$M_{O_3}\phi_{O_3} + M_{O_2}\phi_{O_2} + M_O\phi_O = 1. \quad (17)$$

Additional constraints (Eq. 15) confine the accessible composition space to the triangle shown in Fig. 2. Within this triangle chemical reaction takes place. Any movement off the plane (i.e., in direction of the element vector) is forbidden. The reaction subspace can be spanned by any two

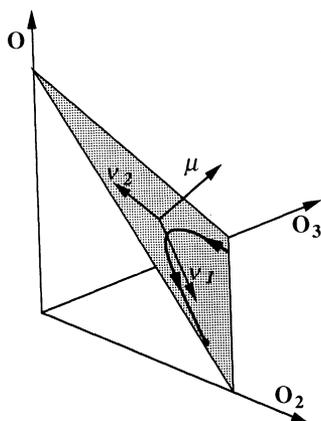


Fig. 2. Schematic illustration of the composition space of a simple  $O_3/O_2/O$  system.

linearly independent reaction vectors. Chemical reaction proceeds according to the chemical rate equations within the subspace (also shown schematically in Fig. 2) until equilibrium is reached, where equilibrium corresponds to one point in the composition space here, that is, in this case equilibrium is a 0-dimensional subspace of the composition space.

### Partial-Equilibrium and Steady-State Assumptions

The partial-equilibrium and steady-state assumptions are commonly used in reduced kinetics schemes. It is helpful to the understanding of the scheme developed here to observe that these assumptions lead to lower-dimensional manifolds in composition space.

Usually reduced mechanisms are developed by assuming the rates in directions of some vectors in composition space to vanish. Thus, for example, partial-equilibrium assumptions force the rates in direction of some reaction vector (namely the one corresponding to the reaction in partial equilibrium) to vanish. Steady-state assumptions force the rate of production of some species to vanish. A detailed discussion of those methods of mechanism reduction in terms of the geometrical representation of chemical kinetics is given in Appendix A.

Although those quasi-steady-state and partial-equilibrium assumptions are quite convenient to use, they have one major disadvantage, namely the explicitly imposed assumption. A case-by-case understanding of different chemical reaction systems is needed in order to develop reduced mechanisms. Depending on the nature of the reaction process, the mixture composition, the temperature range, and so on, different partial-equilibrium or steady-state assumptions have to be specified. Although, for example, a species may be in quasi-steady state within a certain domain of the composition space, the quasi-steady-state assumption might be improper outside this domain. Thus it would be useful to have a scheme, where (given a detailed reaction mechanism) only the desired dimension of the reaction subspace would have to be specified, and the "best assumptions" would be automatically generated by the scheme. Such a method can be developed. It is based on an analysis of the eigenvalues and eigenvectors of

the Jacobian of the system equations and described in the section on the mathematical model.

### The CO/H<sub>2</sub>/Air System

Throughout this article, we use the CO/H<sub>2</sub>/air system to provide specific examples. In this reaction system there are 13 different species (i.e.,  $n_s = 13$ ), which are ordered as follows: N<sub>2</sub>, CO, H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, OH, H, O, HO<sub>2</sub>, CHO, H<sub>2</sub>O<sub>2</sub>, and CH<sub>2</sub>O. Furthermore there are four different elements in the reaction system (i.e.,  $n_e = 4$ ), which are, in order, N, C, H, O. Accordingly there are four different linearly independent element vectors  $\mu_i$  where

$$\mu_N = (2, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0)^T,$$

$$\mu_C = (0, 1, 0, 0, 0, 1, 0, 0, 0, 0, 1, 0, 1)^T,$$

$$\mu_H = (0, 0, 2, 0, 2, 0, 1, 1, 0, 1, 1, 2, 2)^T,$$

$$\mu_O = (0, 1, 0, 2, 2, 1, 2, 1, 0, 1, 2, 1, 2, 1)^T.$$

The detailed reaction mechanism consists of 67 elementary reactions and is listed in Table 1 (see Ref. 19 for references). Thus there are 67 reaction vectors which correspond to elementary reactions. The reaction vectors corresponding to the first six elementary reactions, for example, are given by:

$$\nu_1 = (0, 0, 0, -1, 0, 0, 1, -1, 1, 0, 0, 0, 0)^T,$$

$$\nu_2 = (0, 0, 0, 1, 0, 0, -1, 1, -1, 0, 0, 0, 0)^T,$$

$$\nu_3 = (0, 0, -1, 0, 0, 0, 1, 1, -1, 0, 0, 0, 0)^T,$$

$$\nu_4 = (0, 0, 1, 0, 0, 0, -1, -1, 1, 0, 0, 0, 0)^T,$$

$$\nu_5 = (0, 0, -1, 0, 1, 0, -1, 1, 0, 0, 0, 0, 0)^T,$$

$$\nu_6 = (0, 0, 1, 0, -1, 0, 1, -1, 0, 0, 0, 0, 0)^T.$$

Of course any possible chemical reaction (obeying the law of element conservation) can be expressed by a reaction vector, too.

With the number of species (i.e., the dimension of the composition space)  $n_s = 13$  and four different elements (corresponding to conserved variables), the dimension of the reaction subspace is given by  $n_r = n_s - n_e = 13 - 4 = 9$ . The nitrogen molecule is assumed to be inert, and thus is treated as an element.

The specific system considered in the sample calculations in the mathematical model is a stoichiometric carbon monoxide-hydrogen-air combustion system at pressure of 1 bar with a hydrogen-to-carbon atom mole ratio of 1:10. The specific enthalpy of the system is  $10^6$  J/kg, which corresponds to a temperature of about 400 K for an unburned mixture (only H<sub>2</sub>, O<sub>2</sub>, CO, and N<sub>2</sub> present) and a temperature of about 2430 K for an equilibrium mixture.

### Reaction Trajectories

Let us now look at trajectories in the state space for certain fixed values of enthalpy, pressure and specific element mole numbers (which are in fact constant in homogeneous, adiabatic isobaric systems). Element conservation together with isobaricity and adiabaticity introduces  $2 + n_e$  algebraic constraints into the system of governing equations, namely:

$$\begin{aligned} h &= \text{const}, \\ P &= \text{const}, \\ \chi_j &= \text{const} \quad j = 1, 2, \dots, n_e. \end{aligned} \quad (18)$$

These algebraic constraints define an ( $n_r = n_s - n_e$ )-dimensional linear manifold in the state space, the accessible space for given  $h$ ,  $P$ , and  $\chi_j$ . The significance of this manifold is that if a chemical system has a state corresponding to a point on this manifold, for all times the state of the system is given by a point that is also a point on this manifold. Here one can also see the significance of the element and reaction vectors, which had been defined above: All movements in the state space according to a linear combination of the reaction vectors corresponds to a change of state due to chemical reaction, which means a movement parallel to the manifold. Movements in direction of element vectors correspond to a change of the element composition. They are perpendicular to the manifold and cannot occur if we allow only closed homogeneous systems. Another property of the trajectories on the manifold is that they do not cross (uniqueness of the equation system [20]) and that they all approach one common point, namely the equilibrium point of the system.

Figure 3 shows sample plots of trajectories (obtained from numerical simulations using a de-

TABLE 1

Reaction Mechanism of the CO/H<sub>2</sub>/Air System [19]<sup>a</sup>

		<i>A</i>	$\beta$	<i>E<sub>a</sub></i>
1	O <sub>2</sub> + H → OH + O	2.00 × 10 <sup>14</sup>	0.00	70.3
2	OH + O → O <sub>2</sub> + H	1.47 × 10 <sup>13</sup>	0.00	2.1
3	H <sub>2</sub> + O → OH + H	5.06 × 10 <sup>4</sup>	2.67	26.3
4	OH + H → H <sub>2</sub> + O	2.24 × 10 <sup>4</sup>	2.67	18.4
5	H <sub>2</sub> + OH → H <sub>2</sub> O + H	1.00 × 10 <sup>8</sup>	1.60	13.8
6	H <sub>2</sub> O + H → H <sub>2</sub> + OH	4.46 × 10 <sup>8</sup>	1.60	77.1
7	OH + OH → H <sub>2</sub> O + O	1.50 × 10 <sup>9</sup>	1.14	0.4
8	H <sub>2</sub> O + O → OH + OH	1.51 × 10 <sup>10</sup>	1.14	71.6
9	H + H + M' → H <sub>2</sub> + M'	1.80 × 10 <sup>18</sup>	-1.00	0.0
10	H <sub>2</sub> + M' → H + H + M'	6.98 × 10 <sup>18</sup>	-1.00	436.0
11	H + OH + M' → H <sub>2</sub> O + M'	2.20 × 10 <sup>22</sup>	-2.00	0.0
12	H <sub>2</sub> O + M' → H + OH + M'	3.80 × 10 <sup>23</sup>	-2.00	499.4
13	O + O + M' → O <sub>2</sub> + M'	2.90 × 10 <sup>17</sup>	-1.00	0.0
14	O <sub>2</sub> + M' → O + O + M'	6.78 × 10 <sup>18</sup>	-1.00	496.4
15	H + O <sub>2</sub> + M' → HO <sub>2</sub> + M'	2.30 × 10 <sup>18</sup>	-0.80	0.0
16	HO <sub>2</sub> + M' → H + O <sub>2</sub> + M'	2.66 × 10 <sup>18</sup>	-0.80	206.2
17	HO <sub>2</sub> + H → OH + OH	1.50 × 10 <sup>14</sup>	0.00	4.2
18	OH + OH → HO <sub>2</sub> + H	1.63 × 10 <sup>13</sup>	0.00	158.0
19	HO <sub>2</sub> + H → H <sub>2</sub> + O <sub>2</sub>	2.50 × 10 <sup>13</sup>	0.00	2.9
20	H <sub>2</sub> + O <sub>2</sub> → HO <sub>2</sub> + H	8.39 × 10 <sup>13</sup>	0.00	232.8
21	HO <sub>2</sub> + H → H <sub>2</sub> O + O	3.00 × 10 <sup>13</sup>	0.00	7.2
22	H <sub>2</sub> O + O → HO <sub>2</sub> + H	3.29 × 10 <sup>13</sup>	0.00	232.2
23	HO <sub>2</sub> + O → OH + O <sub>2</sub>	1.80 × 10 <sup>13</sup>	0.00	-1.7
24	OH + O <sub>2</sub> → HO <sub>2</sub> + O	2.67 × 10 <sup>13</sup>	0.00	220.3
25	HO <sub>2</sub> + OH → H <sub>2</sub> O + O <sub>2</sub>	6.00 × 10 <sup>13</sup>	0.00	0.0
26	H <sub>2</sub> O + O <sub>2</sub> → HO <sub>2</sub> + OH	8.97 × 10 <sup>14</sup>	0.00	293.2
27	HO <sub>2</sub> + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	2.50 × 10 <sup>11</sup>	0.00	-5.2
28	OH + OH + M' → H <sub>2</sub> O <sub>2</sub> + M'	3.25 × 10 <sup>22</sup>	-2.00	0.0
29	H <sub>2</sub> O <sub>2</sub> + M' → OH + OH + M'	2.11 × 10 <sup>24</sup>	-2.00	206.8
30	H <sub>2</sub> O <sub>2</sub> + H → H <sub>2</sub> + HO <sub>2</sub>	1.70 × 10 <sup>12</sup>	0.00	15.7
31	H <sub>2</sub> + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + H	9.35 × 10 <sup>11</sup>	0.00	91.2
32	H <sub>2</sub> O <sub>2</sub> + H → H <sub>2</sub> O + OH	1.00 × 10 <sup>13</sup>	0.00	15.0
33	H <sub>2</sub> O + OH → H <sub>2</sub> O <sub>2</sub> + H	2.66 × 10 <sup>12</sup>	0.00	307.6
34	H <sub>2</sub> O <sub>2</sub> + O → OH + HO <sub>2</sub>	2.80 × 10 <sup>13</sup>	0.00	26.8
35	OH + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O	6.80 × 10 <sup>12</sup>	0.00	94.4
36	H <sub>2</sub> O <sub>2</sub> + OH → H <sub>2</sub> O + HO <sub>2</sub>	5.40 × 10 <sup>12</sup>	0.00	4.2
37	H <sub>2</sub> O + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + OH	1.32 × 10 <sup>13</sup>	0.00	143.0
38	CO + OH → CO <sub>2</sub> + H	4.40 × 10 <sup>6</sup>	1.50	-3.1
39	CO <sub>2</sub> + H → CO + OH	6.12 × 10 <sup>8</sup>	1.50	94.1
40	CO + HO <sub>2</sub> → CO <sub>2</sub> + OH	1.50 × 10 <sup>14</sup>	0.00	98.7
41	CO <sub>2</sub> + OH → CO + HO <sub>2</sub>	2.27 × 10 <sup>15</sup>	0.00	349.7
42	CO + O + M' → CO <sub>2</sub> + M'	7.10 × 10 <sup>13</sup>	0.00	-19.0
43	CO <sub>2</sub> + M' → CO + O + M'	1.69 × 10 <sup>16</sup>	0.00	506.4
44	CO + O <sub>2</sub> → CO <sub>2</sub> + O	2.50 × 10 <sup>12</sup>	0.00	200.0
45	CO <sub>2</sub> + O → CO + O <sub>2</sub>	2.55 × 10 <sup>13</sup>	0.00	229.0
46	HCO + M' → CO + H + M'	7.10 × 10 <sup>14</sup>	0.00	70.3
47	CO + H + M' → HCO + M'	1.07 × 10 <sup>15</sup>	0.00	8.6
48	HCO + H → CO + H <sub>2</sub>	2.00 × 10 <sup>14</sup>	0.00	0.0
49	CO + H <sub>2</sub> → HCO + H	1.17 × 10 <sup>15</sup>	0.00	374.4
50	HCO + O → CO + OH	3.00 × 10 <sup>13</sup>	0.00	0.0
51	CO + OH → HCO + O	7.72 × 10 <sup>13</sup>	0.00	366.5
52	HCO + O → CO <sub>2</sub> + H	3.00 × 10 <sup>13</sup>	0.00	0.0
53	CO <sub>2</sub> + H → HCO + O	1.07 × 10 <sup>16</sup>	0.00	463.7
54	HCO + OH → CO + H <sub>2</sub> O	1.00 × 10 <sup>14</sup>	0.00	0.0
55	CO + H <sub>2</sub> O → HCO + OH	2.60 × 10 <sup>15</sup>	0.00	437.7
56	HCO + O <sub>2</sub> → CO + HO <sub>2</sub>	3.00 × 10 <sup>12</sup>	0.00	0.0

TABLE 1

(Continued)

		$A$	$\beta$	$E_a$
57	$\text{CO} + \text{HO}_2 \rightarrow \text{HCO} + \text{O}_2$	$5.21 \times 10^{12}$	0.00	144.5
58	$\text{CH}_2\text{O} + \text{M}' \rightarrow \text{HCO} + \text{H} + \text{M}'$	$1.40 \times 10^{17}$	0.00	320.0
59	$\text{HCO} + \text{H} + \text{M}' \rightarrow \text{CH}_2\text{O} + \text{M}'$	$2.62 \times 10^{15}$	0.00	-56.8
60	$\text{CH}_2\text{O} + \text{H} \rightarrow \text{HCO} + \text{H}_2$	$2.50 \times 10^{13}$	0.00	16.7
61	$\text{HCO} + \text{H}_2 \rightarrow \text{CH}_2\text{O} + \text{H}$	$1.82 \times 10^{12}$	0.00	76.0
62	$\text{CH}_2\text{O} + \text{O} \rightarrow \text{HCO} + \text{OH}$	$3.50 \times 10^{13}$	0.00	14.6
63	$\text{HCO} + \text{OH} \rightarrow \text{CH}_2\text{O} + \text{O}$	$1.12 \times 10^{12}$	0.00	66.0
64	$\text{CH}_2\text{O} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O}$	$3.00 \times 10^{13}$	0.00	5.0
65	$\text{HCO} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{OH}$	$9.71 \times 10^{12}$	0.00	127.6
66	$\text{CH}_2\text{O} + \text{HO}_2 \rightarrow \text{HCO} + \text{H}_2\text{O}_2$	$1.00 \times 10^{12}$	0.00	33.5
67	$\text{HCO} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$	$1.32 \times 10^{11}$	0.00	17.3

<sup>a</sup>  $A$  in cm/mol/s;  $E_A$  in kJ/mol;  $k = AT^\beta \exp(-E_A/RT)$ .

Collision efficiencies  $f_{\text{H}_2} = 1.00$ ,  $f_{\text{O}_2} = 0.35$ ,  $f_{\text{H}_2\text{O}} = 6.50$ ,  $f_{\text{N}_2} = 0.50$ ,  $f_{\text{CO}} = 1.50$ ,  $f_{\text{CO}_2} = 1.50$ .

tailed reaction mechanism, which can be found, e.g., in Ref. 19) for the water-gas system for the specific values of pressure, enthalpy, and element composition described in the previous section. Plotted are projections into the  $\text{CO}_2/\text{H}_2\text{O}$  and the  $\text{CO}_2/\text{OH}$  planes, respectively (it should be noted that this projection leads to some lines that cross, which by no means corresponds to a crossing of trajectories). Chemical reaction can be regarded as a movement along those trajectories.

### Attracting Manifolds

There is one notable feature that can be seen in Fig. 3, namely the fact that trajectories tend to "bunch" and approach one another far before equilibrium is reached. It looks as if there is a low-dimensional manifold (represented by a line in this two-dimensional projection) that has the property that all trajectories tend to approach that manifold, and that on this manifold only slow time scales govern the chemical reaction. In other words, even systems with quite different initial conditions approach common attracting manifolds.

This observation leads to the central question addressed in this article: Are there low-dimensional attracting manifolds in the state space that have the property that if a trajectory is near the manifold, it will remain close to it for all times? We answer this question in the affirmative, and show how such manifolds can be determined and used to simplify chemical kinetics.

## MATHEMATICAL MODEL

### General Idea

The behavior of a chemical reaction system can be well understood if one looks at distinct points in the state space and analyzes the behavior in the neighborhood. Let us assume that we apply a small perturbation to the system. How will it respond? The answer can be provided by a modal analysis (Appendix B), which describes the behavior of the system in a linearized neighborhood of some point in the state space in terms of an analysis of the eigenvalues and eigenvectors of the Jacobian of the governing equation system. This analysis reveals that there are  $n_s$  characteristic time scales (given by the eigenvalues of the Jacobian) associated with  $n_s$  characteristic directions (the corresponding eigenvectors). Now there are three principal possibilities how a system can react to a perturbation, shown schematically in Fig. 4:

1. If we perturb in the direction of an eigenvector whose eigenvalue has a positive real part, the perturbation will increase.
2. If we perturb in the direction of an eigenvector whose eigenvalue is zero (this usually corresponds to a change of a conserved variable), the perturbation will not change with time.
3. If we perturb in the direction of an eigenvector whose eigenvalue has a negative real part, the perturbation will relax to zero.

It shall be noted that in this example many simplifications had been made (linearization, etc.),

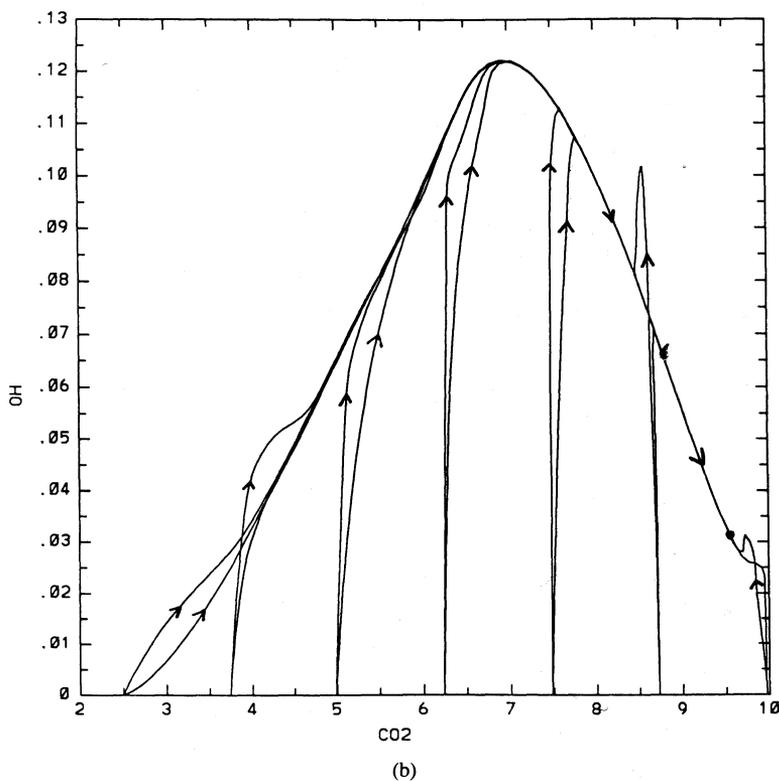
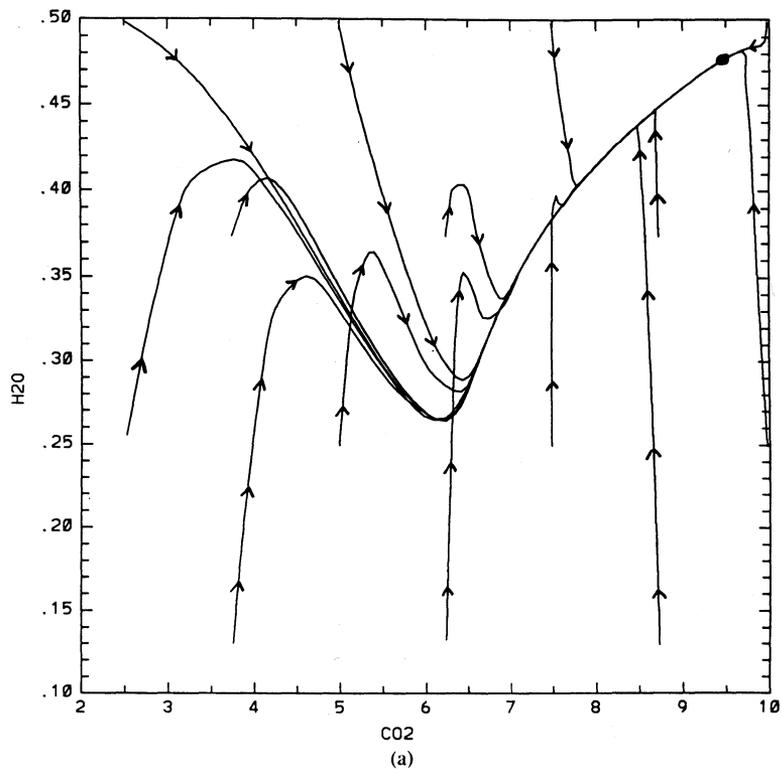


Fig. 3. Sample trajectories in the state space for a  $\text{CO}/\text{H}_2/\text{air}$  system.  $\bullet$  denotes the equilibrium value. (a) Projection into the  $\text{CO}_2$ - $\text{H}_2\text{O}$  plane. (b) Projection into the  $\text{OH}$ - $\text{CO}_2$  plane.

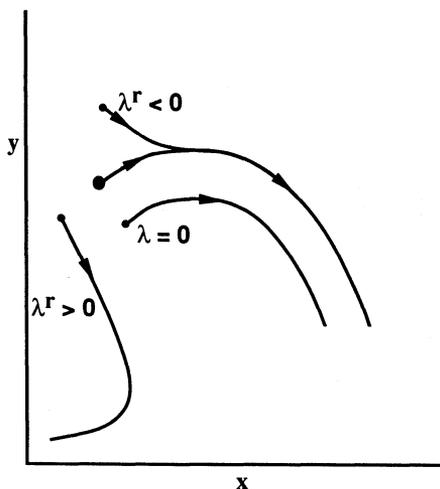


Fig. 4. Schematic illustration of the behavior of a dynamical system.

but nevertheless it gives an idea of the behavior of real systems. If we look at real chemical systems, sample calculations for a  $\text{CO}/\text{H}_2/\text{O}_2$  combustion system show the following: Some eigenvalues are zero, namely those corresponding to the eigenvectors that can be expressed as linear combinations of the element vectors (this can also be shown analytically). Almost all other eigenvalues are negative with values from typically  $-10^{-2}$  to  $-10^7 \text{ s}^{-1}$ . Only very few eigenvalues are positive (in the sample calculations at most one eigenvalue was positive). At the equilibrium point all eigenvalues are zero or negative.

Because in chemical reactions a large number of the eigenvalues have large negative values (for an isothermal system, for example, it can be easily shown that the sum of the eigenvalues is always negative), many perturbations of a state (that could be induced, for example, by molecular diffusion) lead to some sort of fast relaxation (which indeed need not lead to the initial state). Furthermore the example (together with Fig. 3) shows that many different initial conditions after some short time (in fact the time scale associated with the smallest eigenvalues) can lead to movements within one common subspace of the composition space.

Further insight is obtained if we look at the time development of a linearized system in the neighborhood of some state  $\phi^0$ . In Appendix C it is shown for a linearized system that if we identify in the composition space the points where the system is in equilibrium with respect to the fastest

time scales (i.e., the rates in direction of the eigenvectors with the smallest eigenvalues is zero), we obtain a subspace of the composition space in which all movements correspond to slow time scales. States that are not in this subspace evolve rapidly in time in direction of this subspace.

The consequences for general systems are as follows: If a subspace in the composition space can be found where the system is "in equilibrium" with respect to its smallest  $m$  eigenvectors, this subspace defines a low-dimensional manifold that is characterized by the fact that movements along it are associated with slow time scales and can be used to simplify chemical kinetics.

### Mathematical Model

In the previous section it was shown (for simple examples) that based on an eigenvector analysis of the governing equations in a homogeneous chemical reaction system, it is possible to identify some low-dimensional subspaces of the composition space that may be used to simplify the description of complicated chemical systems. This section outlines how the above considerations can be used to construct a method that, given a detailed reaction mechanism, defines a low-dimensional manifold in the state space with the property that all the movements on this manifold represent slow time-scale processes, and that systems with initial states that do not lie on this manifold evolve rapidly in time in the direction of the manifold.

Consider a chemical reaction system with the governing equations

$$\frac{\partial h}{\partial t} = 0, \quad (7)$$

$$\frac{\partial P}{\partial t} = 0, \quad (8)$$

$$\frac{\partial \phi_i}{\partial t} = \frac{\dot{\omega}_i(h, P, \phi)}{\rho(h, P, \phi)} \quad i = 1, 2, \dots, n_s, \quad (9, 10)$$

or, written in terms of vectors,

$$\frac{\partial \psi}{\partial t} = \mathbf{F}(\psi), \quad (19)$$

with  $\psi = (h, P, \phi_1, \phi_2, \dots, \phi_{n_s})^T$ .

For each point in the state space, the eigenvalues of the Jacobian  $F_\psi$  (with components  $\partial F_i / \partial \psi_j$ ) identify the  $n_s + 2$  different time scales associated with the movement in the state space. The corresponding eigenvectors describe the "characteristic directions" associated with those time scales. Now the general idea is to look for points in the state space for which components in the directions of certain eigenvectors (in this case those associated with fast time scales) vanish. Because the occurrence of degenerate eigenvalues can complicate the analysis, it is useful to work in a modified eigenvector basis. This modified local basis shall be given as follows: The eigenvectors corresponding to distinct eigenvalues, as well as linearly independent eigenvectors corresponding to a multiple eigenvalue form basis vectors. If an eigenvalue of multiplicity  $m$  has less than  $m$  linearly independent eigenvectors, or if there is a complex pair of eigenvalues, the vectors, which span the corresponding invariant subspace, shall form basis vectors.

In this way it is possible to construct a basis that spans the whole space of dimension  $n = n_s + 2$ . Now define an  $n_c$ -dimensional manifold in reaction space by the condition that the components of the movement in the direction of  $n_f = n_r - n_c$  distinct basis vectors vanish. In other words, given the modified basis of eigenvectors  $V$ , where  $V$  is a matrix with a column partitioning given by the vectors  $v_i$  of the modified eigenvector basis, ordered according to decreasing values of the real parts of the corresponding eigenvalues

$$V = \begin{pmatrix} | & | & & | \\ v_1 & v_2 & \cdots & v_n \\ | & | & & | \end{pmatrix}, \quad (20)$$

and its inverse  $V^{-1}$ :

$$V^{-1} = \begin{pmatrix} \text{---} & \tilde{v}_1 & \text{---} \\ \text{---} & \tilde{v}_2 & \text{---} \\ & \vdots & \\ \text{---} & \tilde{v}_n & \text{---} \end{pmatrix}, \quad (21)$$

the equation system

$$WF(\psi) = 0 \quad (22)$$

defines the low-dimensional manifold, where  $W$

is the  $n_f$ -by- $n$  matrix

$$W = \begin{pmatrix} \text{---} & \tilde{v}_{2+n_e+n_c+1} & \text{---} \\ \text{---} & \tilde{v}_{2+n_e+n_c+2} & \text{---} \\ & \vdots & \\ \text{---} & \tilde{v}_n & \text{---} \end{pmatrix}, \quad (23)$$

(i.e.,  $W$  is the matrix formed by the last  $n_f$  rows of the inverse of the matrix of basis vectors). In this way we define an  $n_c = n_r - n_f$ -dimensional manifold in the reaction space with the property that for all points on this manifold, the components of the velocity in direction of the eigenvectors corresponding to the  $n_f$ -most negative eigenvalues vanish. Roughly speaking this manifold represents states that are "in equilibrium with respect to the fastest relaxing time scales." However, there is the possibility of some arbitrariness in the formulation, namely if either the eigenvalues  $\lambda_{2+n_e+n_c}$  and  $\lambda_{2+n_e+n_c+1}$  form a complex pair or if  $\lambda_{2+n_e+n_c} = \lambda_{2+n_e+n_c+1}$ . In those cases the construction of the manifold can depend on the choice of the modified basis vectors.

The formulation above would allow the construction of a low-dimensional manifold. However, due to poor conditioning (roughly speaking, "nearly linearly-dependent eigenvectors"), numerical difficulties could arise [21]. Thus it is useful to work in terms of another basis, the basis of the so-called real Schur vectors [21]. It can be shown that the formulation in this basis is equivalent to the formulation above. Furthermore, the basis of real Schur vectors can be easily computed [21] and it has the advantage of being orthogonal. Following this approach, the low-dimensional manifold is constructed as follows:

Let  $Q^T F_\psi Q = N$  denote the real Schur decomposition of the Jacobian, such that the eigenvalues  $\lambda_i$  appear in the diagonal of  $N$  (or in the 2-by-2 blocks in case of complex pairs) in the order of descending real parts. (Such a Schur decomposition always exists and can be calculated efficiently using a modification of the algorithm in Ref. 22.) If  $Q$  is written as

$$Q = \begin{pmatrix} | & | & & | \\ q_1 & q_2 & \cdots & q_n \\ | & | & & | \end{pmatrix}, \quad (24)$$

with  $q_i$  being the Schur vectors, then the low-dimensional manifold is defined as the set of

points in the state space for which

$$0 = Q_L^T(\psi)F(\psi)$$

$$= \begin{pmatrix} \text{---} & q_{2+n_e+n_c+1}^T & \text{---} \\ \text{---} & q_{2+n_e+n_c+2}^T & \text{---} \\ & \vdots & \\ \text{---} & q_n^T & \text{---} \end{pmatrix} F(\psi). \quad (25)$$

$Q_L^T$  denotes the  $n_f$ -by- $n$  matrix, whose row partitioning are the transpose of the Schur vectors  $q_i$  with  $i = 2 + n_e + n_c + 1, 2 + n_e + n_c + 2, \dots, n$ , or, in other words  $Q_L^T$  is the matrix that is obtained from  $Q^T$  by omitting the first  $2 + n_e + n_c$  rows, namely the rows corresponding to the conserved and the slowly changing variables.

From this construction it can be seen that there is one major difference compared with conventional reduced mechanisms, namely the fact that the only restriction imposed on the system is the choice of the dimension  $n_c$  of the manifold in the reaction space.

### Numerical Solution

After the formulation for the construction of the low-dimensional manifold has been given, there is need for a numerical method that allows the computation. In general, the manifold in the reaction subspace can (at least piecewise) be parametrized by  $n_c (= n_r - n_f)$  coordinates.

Thus together with Eq. 25,  $2 + n_e + n_c$  parameters define the low-dimension manifold in the state space. The task of identifying the low-dimensional manifold consists of solving the parameter equations

$$G(\psi, \tau) = \begin{pmatrix} Q_L^T(\psi)F(\psi) \\ P(\psi, \tau) \end{pmatrix} = 0, \quad (26)$$

with  $P(\psi, \tau)$  being  $2 + n_e + n_c$  additional parameter equations necessary to complete the equation system. The choice of those equations influences problems of existence and uniqueness of a solution to Eq. 26, but not the construction of the manifold itself. Because we are treating closed, adiabatic, isobaric systems here,  $2 + n_e$  of the parameter equations are readily obtained, namely

by specifying

$$0 = h - \tau_h,$$

$$0 = P - \tau_P,$$

$$0 = \chi_i(\phi) - \tau_{\chi_i}, \quad i = 1, 2, \dots, n_e, \quad (27)$$

that is, by using the equations fixing enthalpy, pressure, and element composition. The choice of the remaining  $n_c$  parameter equations cannot be performed in such an easy way in order to guarantee existence and uniqueness.

To summarize, in order to obtain the manifold, we now have to solve the equation system

$$0 = Q_L^T(\psi)F(\psi), \quad (28)$$

$$0 = g(\psi, \tau_e), \quad (29)$$

$$0 = h(\psi, \tau_c), \quad (30)$$

where Eq. 28 gives the definition equations for the manifold, Eq. 29 the parameter equations that fix the conserved variables, and Eq. 30 the remaining parameter equations, which have yet to be specified. The parameters  $\tau_c$  and the corresponding equations can be chosen quite arbitrarily and may, for example, be the temperature, specific mole numbers, specific element mole numbers, concentrations, or even linear combinations of them. Their definition has no influence on the manifold itself, but only allows some parametrization. If we use specific mole numbers in order to parametrize the manifold, this corresponds to a projection of the manifold onto coordinates in the natural basis of the state space. The equation system 30 then reads

$$\phi_i - \tau_{\phi_i} = 0 \quad (31)$$

for  $n_c$  specific species.

Now after the equation system has been completed, there are several ways of finding solutions. The simplest way is to look for solutions for fixed values of the parameters, that is, solve Eq. 26 by Newton's method.

In order to illustrate this, let us take the CO/H<sub>2</sub>/air combustion system as an example. Using detailed chemistry, the dimension of the governing ordinary differential equation system is 15, with the enthalpy  $h$ , the pressure  $P$ , and the specific mole numbers of the species H<sub>2</sub>, CO, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, H, O, OH, HO<sub>2</sub>, HCO,

$\text{CH}_2\text{O}$ , and  $\text{H}_2\text{O}_2$  as dependent variables. Because the reaction system is said to be closed, adiabatic, homogeneous, and isobaric, there are six conserved variables, namely, the pressure, the enthalpy, and the specific element mole numbers of H, O, C, and N. Thus the dimension of the reaction space is  $n - n_e - 2 = 9$ . If we want to reduce the dimension of the reaction space to let us say two, two parameters have to be defined. The choice is quite arbitrary; thus assume that the specific mole numbers of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are the parameters. In this way we would end up with the equation system

$$\begin{aligned} 0 &= h - \tau_h, \\ 0 &= P - \tau_P, \\ 0 &= \chi_H(\phi) - \tau_H, \\ 0 &= \chi_O(\phi) - \tau_O, \\ 0 &= \chi_C(\phi) - \tau_C, \\ 0 &= \chi_N(\phi) - \tau_N, \\ 0 &= \phi_{\text{H}_2\text{O}} - \tau_{\text{H}_2\text{O}}, \\ 0 &= \phi_{\text{CO}_2} - \tau_{\text{CO}_2}, \\ 0 &= Q_L^T F(\psi), \end{aligned} \quad (32)$$

which, for given reference values  $\tau$ , calculates points that lie on the manifold. This defines a two-dimensional manifold in the reaction space with the reaction progress variables being  $\phi_{\text{H}_2\text{O}}$  and  $\phi_{\text{CO}_2}$ . If this equation system is solved for varying values of the parameters, a table of points on the low-dimensional manifold is obtained. Certain difficulties may arise, however, depending on the choice of parameters, which can be seen from Fig. 5. It shows an arbitrary example for a one-dimensional manifold in a two-dimensional space. If  $x$  is chosen as a parameter, in some domains a unique mapping could not be defined. However, if we choose  $y$  as the parameter, the problem is easily solved in this example. Another problem is that the theoretically accessible values for the parameters do not necessarily need to be values for which points on the manifold exist. This can be seen from a simple example. Consider the  $\text{CO}/\text{H}_2/\text{air}$  system discussed above. Theoretically (assuming a stoichiometric mixture) all hydrogen could be present as  $\text{H}_2\text{O}$ . But at high temperatures the construction of the

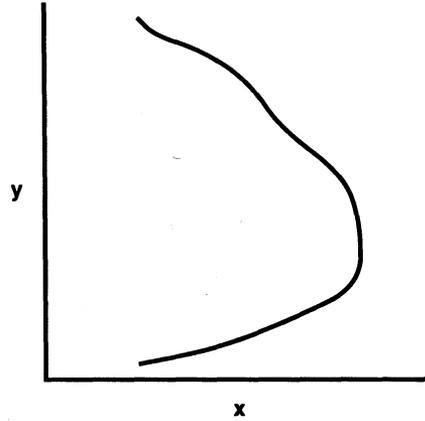


Fig. 5. Mapping of a one-dimensional manifold.

manifold would always determine a certain amount of hydrogen which appears as H or OH. All those problems can be easily avoided because the choice of the parametrization does not influence the construction of the manifold. Thus arc-length continuation methods can be used to solve Eq. 26 [27].

In this work we use several different approaches to solve Eq. 26. Usually, the solution is performed by Newton's method. In case of convergence problems due to bad initial guesses, an iterative approach is used. It can be outlined as follows:

Start with an initial guess of the state variables  ${}^0(h, P, \phi)$  that fulfills the algebraic equations  $P(\psi, \tau)$  of Eq. 26.

For  $i = 0, 1, 2, \dots$

Compute the Jacobian  ${}^i F_\psi$  of the governing equation system and the Real Schur decomposition  ${}^i Q^T {}^i F_\psi {}^i Q = N$  for given  ${}^i \psi = {}^i(h, P, \phi)$ . Solve

$$P(\psi, \tau) = 0, \quad (33)$$

$${}^i Q_L^T \frac{d\psi}{dt} = {}^i Q_L^T F(\psi), \quad (34)$$

until a steady state is obtained.

If  $\|{}^{i+1}\psi - {}^i\psi\| < \epsilon$  accept solution, set  $\psi = {}^{i+1}\psi$  and leave loop.

The solution of the differential/algebraic equation system 33–34 is performed by an extrapolation method [23, 24].

Additionally, if problems in the parametrization occur as described above, the arc-length

continuation methods ALCON1 [28] or PITCON [29] can be used.

However, it would be desirable to develop a general procedure, that is, a general arc-length continuation method with an arbitrary number of parameters, capable of avoiding those problems in the numerical solution.

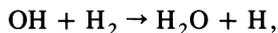
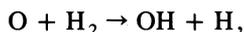
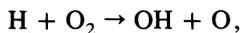
## RESULTS

Given a detailed reaction mechanism, the method presented so far allows the automatic generation of low-dimensional manifolds in composition space, which can be used to obtain simplified models for chemical reaction systems. In order to show the validity of the approach, sample calculations for low-dimensional manifolds, as well as for trajectories in the state space have been performed. The system considered here is a carbon monoxide-hydrogen-air combustion system that has been discussed in detail in a previous section. Calculations using the method described in this article are performed in order to determine one- and two-dimensional manifolds in the reaction space. The reason for the restriction to such low dimensions is only because of problems in the visualization of the results. Higher-dimensional manifolds can easily be calculated, too. Sample trajectories are calculated by solving the system of governing equations for an adiabatic, isobaric, homogeneous closed reaction system for varying initial conditions. Details can be found in Refs. 18 or 25. All calculations (low-dimensional manifold as well as sample trajectories) are based on a detailed reaction mechanism consisting of 13 species and 67 elementary reactions listed in Table 1 (see, e.g., Ref. 19 for details and further references).

### One-Dimensional Manifolds

A comparison of one-dimensional manifolds in the reaction space obtained by the method described in this article with manifolds obtained from a conventional reduced mechanism has been performed in order to point out the difference between these two methods. The reaction progress variable is chosen to be the specific mole number of  $\text{CO}_2$ . The conventional reduced mechanism is obtained in the following way: For points on the calculated one-dimensional manifold in the state

space an analysis of the reaction mechanism is performed, that is, based on a detailed mechanism [19], the reactions that are in partial equilibrium as well as the species that are in quasi-steady-state are determined. The results are used to form the algebraic constraints needed to construct the manifold. At the conditions that are investigated,  $\text{HO}_2$ ,  $\text{HCO}$ ,  $\text{CH}_2\text{O}$ , and  $\text{H}_2\text{O}_2$  are almost in quasi-steady-state, and the reactions



are more or less in partial equilibrium. Using those constraints, the compositions on the manifold for the reduced mechanism are calculated using Newton's method.

In this way, for fixed values of the enthalpy, the pressure, and the element mass fractions, all other state variables are explicitly given as functions of the reaction progress variable alone.

Figures 6a and 6b show examples of this mapping for the specific mole numbers of  $\text{H}_2\text{O}$  and  $\text{H}$ . It can be seen that at temperatures higher than about 1700 K (corresponding to a specific mole number for  $\text{CO}_2$  of about 6 for this particular mixture) the two manifolds agree quite well. Below this temperature there seems to be a change of the reaction paths that cannot be accounted for by the quasi-steady-state and partial equilibrium assumptions made in the conventional reduced mechanism. In order to show that the manifold obtained by the above method describes the reaction system better than the one obtained with the conventional reduced mechanism, sample calculations of trajectories in the state space (based on a detailed reaction mechanism [19]) are performed. Many different initial conditions are used, corresponding to pure mixtures of  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$  as well as to mixtures with large amounts of hydrogen atoms added. Plots of the two manifolds together with the trajectories are shown in Figs. 7a and 7b. Plotted are the specific mole numbers of  $\text{H}_2\text{O}$  and  $\text{H}$  versus the reaction progress variable (specific mole number of  $\text{CO}_2$ ), respectively. It can be seen that the trajectories approach the manifold, which is calculated using the method described in this article. Even in

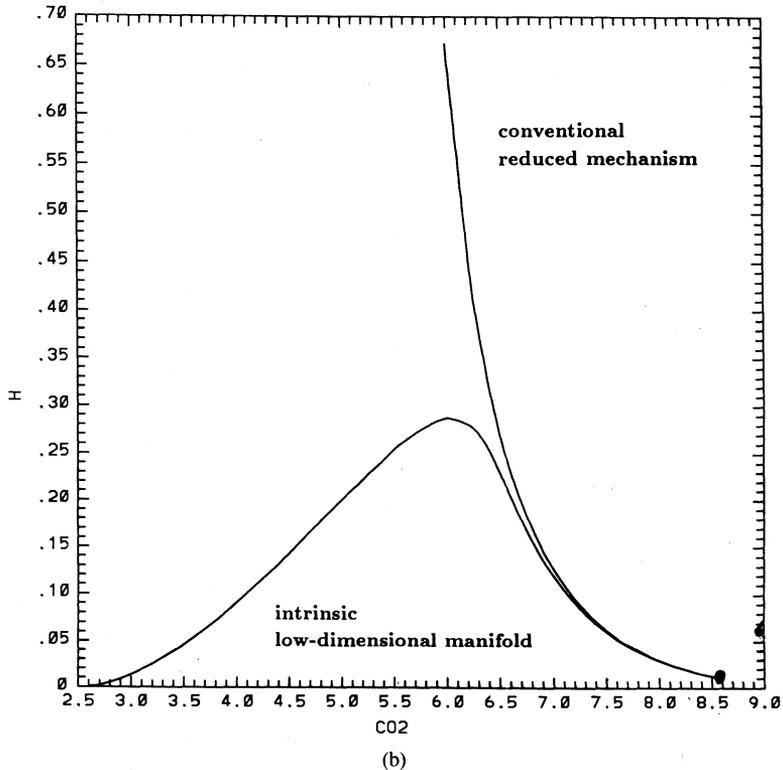
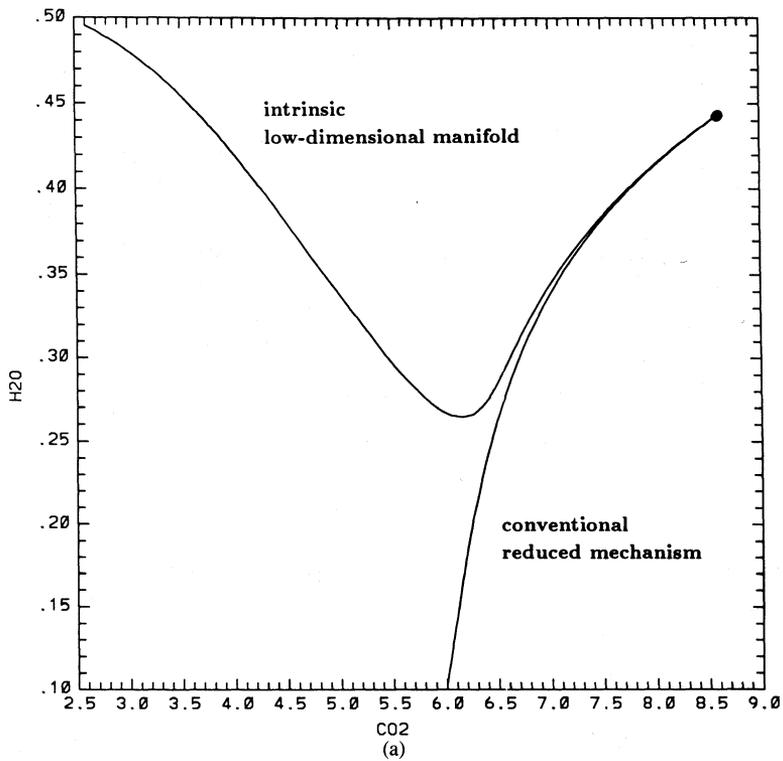


Fig. 6. (a) Plot of the one-dimensional manifold for the specific mole number of  $\text{H}_2\text{O}$ . ● denotes the equilibrium value. (b) Plot of the one-dimensional manifold for the specific mole number of  $\text{H}$ . ● denotes the equilibrium value.

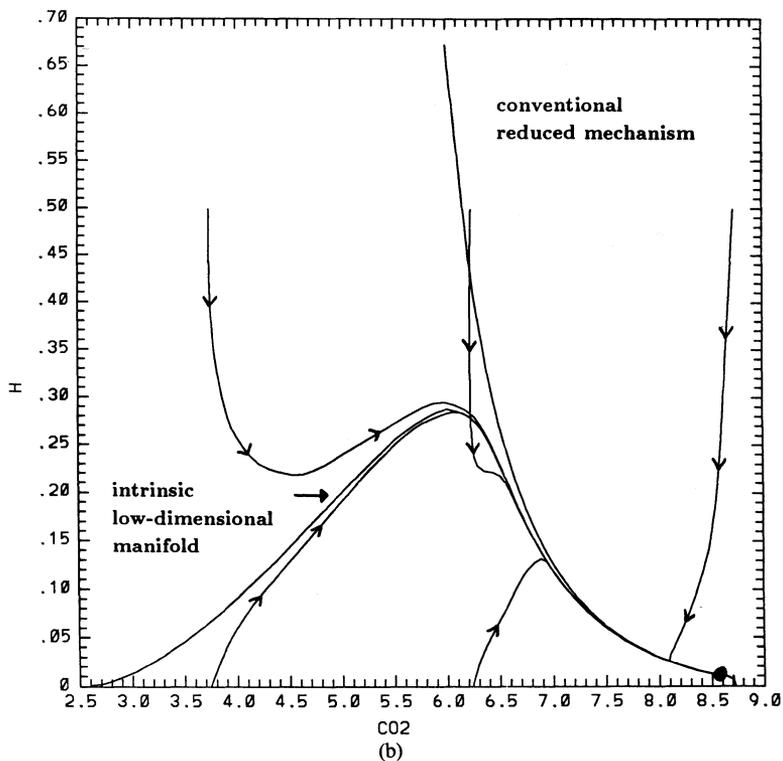
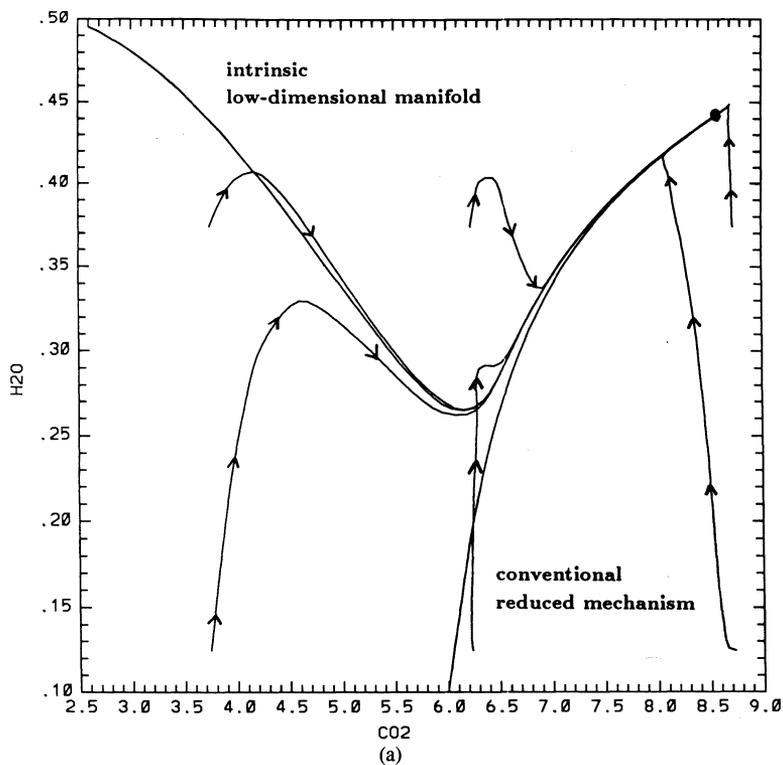


Fig. 7. (a) Plot of the one-dimensional manifold for the specific mole number of  $\text{H}_2\text{O}$  together with sample trajectories.  $\bullet$  denotes the equilibrium value. (b) Plot of the one-dimensional manifold for the specific mole number of  $\text{H}$  together with sample trajectories.  $\bullet$  denotes the equilibrium value.

regions (low temperatures) where a conventional reduced mechanism with such a small number of steps fails, the manifold describes the reaction system quite well.

One aspect that those pictures do not show is the speed with which the trajectories approach the low-dimensional manifold. In fact (as is shown later for examples with two reaction progress variables) it only takes a short time for the trajectories to approach the manifold, compared with the time associated with the following movement along the manifold. One further effect can be seen in the plots. In regions of low temperatures, the trajectories approach the manifold, but only "merge" with it as soon as the temperature increases. Thus it might be necessary to take into account another reaction progress variable (increasing the dimension of the reaction space to two) at low temperatures. In fact, calculations show (see below) that the low-temperature range can be described much better if two reaction progress variables are defined.

### Two-Dimensional Manifolds

For the two-dimensional manifolds in the reaction space the specific mole numbers of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  have been chosen as parameters. Thus (given specific values for the enthalpy, the pressure, and the specific element mole numbers) the numerical method provides values for the specific mole numbers of all species as functions of  $\phi_{\text{CO}_2}$  and  $\phi_{\text{H}_2\text{O}}$ . The results then can be visualized in a three-dimensional plot of the chosen variable versus the two reaction progress variables.

Figures 8a and 8b show plots of the two-dimensional manifolds for the specific mole numbers of H and OH, respectively. However, the method produces such manifolds for all the different species in the reaction system. In addition to the two-dimensional manifolds (represented by the nets of lines), the one-dimensional manifolds (described above), which lie on the two-dimensional manifolds, have been plotted and can be seen as lines on the surfaces. There are several important features that should be mentioned: First the manifolds are nonlinear. This can be expected, because the chemistry introduces nonlinear terms in the governing equation system. Far more interesting is the fact that there exist local maxima and minima in the plots (e.g., the minimum in the plot of the OH specific mole num-

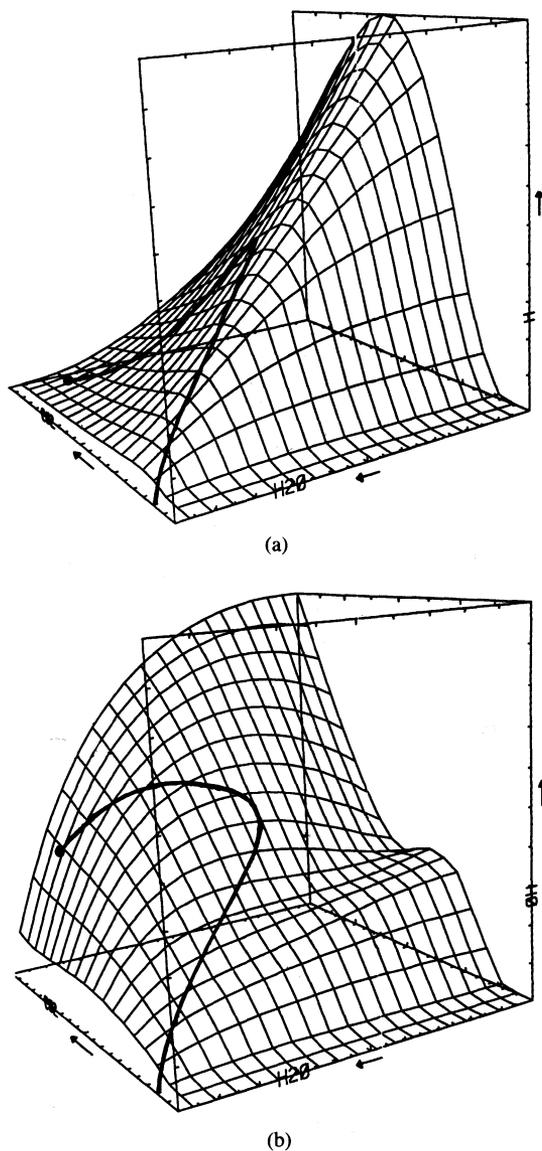


Fig. 8. (a) Plot of the two-dimensional manifold for the specific mole number of H. ● denotes the equilibrium value. Plotted are specific mole numbers in the range of 1.85–9.32 for  $\text{CO}_2$ , 0.096–0.496 for  $\text{H}_2\text{O}$ , 0.0–0.855 for H. The arrows at the axes denote increasing values of the variables. ● denotes the equilibrium value. (b) Plot of the two-dimensional manifold for the specific mole number of OH. ● denotes the equilibrium value. Plotted are specific mole numbers in the range of 1.85–9.32 for  $\text{CO}_2$ , 0.096–0.496 for  $\text{H}_2\text{O}$ , 0.0–0.224 for OH. The arrows at the axes denote increasing values of the variables. ● denotes the equilibrium value.

bers). In these regions there seems to be a change of the reaction paths governing the chemical kinetics, which is recognized by the method.

In the same way as for the one-dimensional manifolds, the significance of these manifolds is

best understood if the plots of sample trajectories in the state space are added. Figures 9a and 9b show plots of the two-dimensional manifolds together with sample trajectories for the specific mole numbers of H and OH, respectively. The sample trajectories start at very different initial

conditions and are calculated using a detailed reaction mechanism as described above. Plotted are not only the trajectories, but also their projections (in direction of the vertical axes) on the manifold. Thus the trajectories merge with the manifold where the two curves (trajectories and projection) merge. Additionally vertical bars have been included between the trajectories and the projections. These verticals represent equidistant time steps of  $10 \mu\text{s}$  on the trajectories. Thus, if there are, say, ten vertical bars between the initial state of the trajectory and the point where it merges with the manifold, this would correspond to a time of  $100 \mu\text{s}$  that is necessary for the trajectory to approach the manifold.

Furthermore the improvement made by using a two-dimensional instead of a one-dimensional manifold can be seen in Fig. 9. The trajectories merge with the manifold much faster than the different trajectories merge. Thus it should be expected that the results would further improve if a three-dimensional manifold were used.

The figures above showed that, for very differing initial conditions, trajectories in the state space approach rapidly the low-dimensional manifold. The rate of approaching depends on the time scales (eigenvalues) that are associated with the eigenvectors that have been used to construct the "equilibrium condition" of the manifold. If, for example, we consider the  $\text{CO}/\text{H}_2/\text{O}_2/\text{N}_2$  system, there are 15 time scales (i.e., eigenvalues) at each point in the state space. Six of them are zero (those corresponding to conserved variables). There are nine remaining eigenvalues corresponding to chemical reactions (the corresponding eigenvectors are linear combinations of reaction vectors). If two additional parameters are specified ( $\text{CO}_2$  and  $\text{H}_2\text{O}$  in our case), the two largest time scales are associated with movements parallel to the manifold. The largest of the remaining seven eigenvalues then corresponds to the slowest time scale of movements in the direction of the manifold and gives an idea of the speed with which states near the low-dimensional manifold approach the manifold.

One possibility to quantify those results is to define some mapping between points of the trajectories and corresponding points on the manifold. The definition of such a mapping is quite arbitrary, and because we are mainly interested only in the time it takes for the trajectory to approach

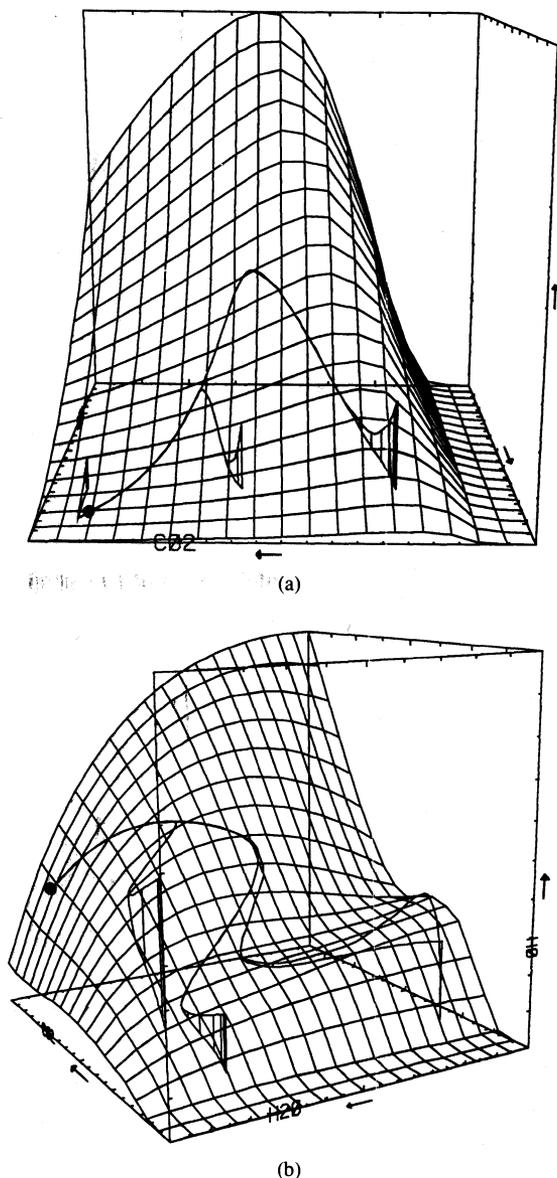


Fig. 9. (a) Plot of the two-dimensional manifold together with sample trajectories for the specific mole number of H. ● denotes the equilibrium value. Plotted are specific mole numbers (scaling as in Fig. 8a). (b) Plot of the two-dimensional manifold together with sample trajectories for the specific mole number of OH. ● denotes the equilibrium value. Plotted are specific mole numbers (scaling as in Fig. 8b).

the manifold, we can make a simple choice. In this work the mapping has been simply defined as the vertical projection of the trajectory onto the manifold. Thus, for example,  $\phi_{\text{OH}}^{\text{tr}}(\phi_{\text{CO}_2}, \phi_{\text{H}_2\text{O}})$  denotes the value of the specific mole number of OH on the trajectory for given values of the parameters  $\phi_{\text{CO}_2}$  and  $\phi_{\text{H}_2\text{O}}$ ,  $\phi_{\text{OH}}^{\text{man}}(\phi_{\text{CO}_2}, \phi_{\text{H}_2\text{O}})$  denotes the corresponding value on the manifold. Values for the trajectories and the corresponding values on the low-dimensional manifold have been calculated for various trajectories, and the results have been plotted in Fig. 10 for the specific mole numbers of the hydroxy-radicals. Figure 10a shows a long time scale, including part of the time interval of relaxation to equilibrium. In this case in fact the curves of the trajectories and of the corresponding projections on the manifold cannot be distinguished, which shows that in this time interval the low-dimensional manifold is a good approximation for the chemical reaction system, that is, the trajectories have already approached the manifold. Figure 10b simply shows a much shorter time interval, namely at the beginning of the reaction. Here it can be seen that although trajectories and the corresponding values of the low-dimensional manifold start at different initial values, after a short time (at most 0.1 ms) the curves (and thus the trajectory and the manifold) merge.

Figure 11 finally shows a plot of the error defined by

$$\epsilon = \frac{\phi_{\text{OH}}^{\text{man}}(\phi_{\text{CO}_2}, \phi_{\text{H}_2\text{O}}) - \phi_{\text{OH}}^{\text{tr}}(\phi_{\text{CO}_2}, \phi_{\text{H}_2\text{O}})}{\phi_{\text{OH}}^{\text{man}}(\phi_{\text{CO}_2}, \phi_{\text{H}_2\text{O}})}$$

as a function of time. In this case the initial error is 100%, because the mixtures considered in the calculation of the trajectories are all mixtures with no OH present in the initial state. The error decreases rapidly after a short time (depending on the initial conditions of the trajectories), corresponding to the time needed for the trajectories to approach the manifold. It is emphasized again that the definition of the distance and thus the error is quite arbitrary, but convenient. A more sophisticated way to define the error could be based on a projection of the states of the trajectories on the manifold in direction of the trajectory.

These examples show that (together with the knowledge of the eigenvalues at specific points in

the state space) sample calculations of trajectories can provide information about the quality of the approximation by the low-dimensional manifold.

## DISCUSSION

The examples above have shown that the method of constructing intrinsic low-dimensional manifolds in composition space presented in this article provides a useful method for reducing chemical kinetics. In applications, tabulated values of the manifold as functions of some parameters can be used to reduce the dimension of the composition space remarkably. This can be especially useful for pdf calculations of turbulent reacting flows, where the dimension of the composition space determines the number of independent variables in the transport equation for the joint pdf [14, 15].

There are several advantages of the method in comparison to conventional reduced mechanisms (based on quasi-steady-state and partial-equilibrium assumptions). In the method presented in this article the “reduction” of the mechanism (and of the dimension of the state space) is performed automatically, based on a detailed reaction mechanism. The only imposed restriction is the dimension of the manifold. Thus very large reaction systems can be handled, which is important, because current detailed mechanisms for combustion processes involve up to 600 species and 2500 reactions [26]. Furthermore (apart from the need of a detailed mechanism), no “chemical knowledge” has to be incorporated into the model. In fact the method itself can produce information about the chemistry. Together with the construction of the low-dimensional manifold, information about the characteristic time scales (eigenvalues) and corresponding characteristic directions (eigenvectors) is obtained. At every point on the low-dimensional manifold, the method can identify the elementary reactions associated with the different time scales. (This analysis has been added to the method, but not been discussed in this article.)

In contrast to other reduced mechanisms our method does not provide simple closed-form expressions for the chemical kinetics. The basic closed-form analytic equations for the low-dimensional manifold are too complicated to be used directly. Therefore we solve the equations in

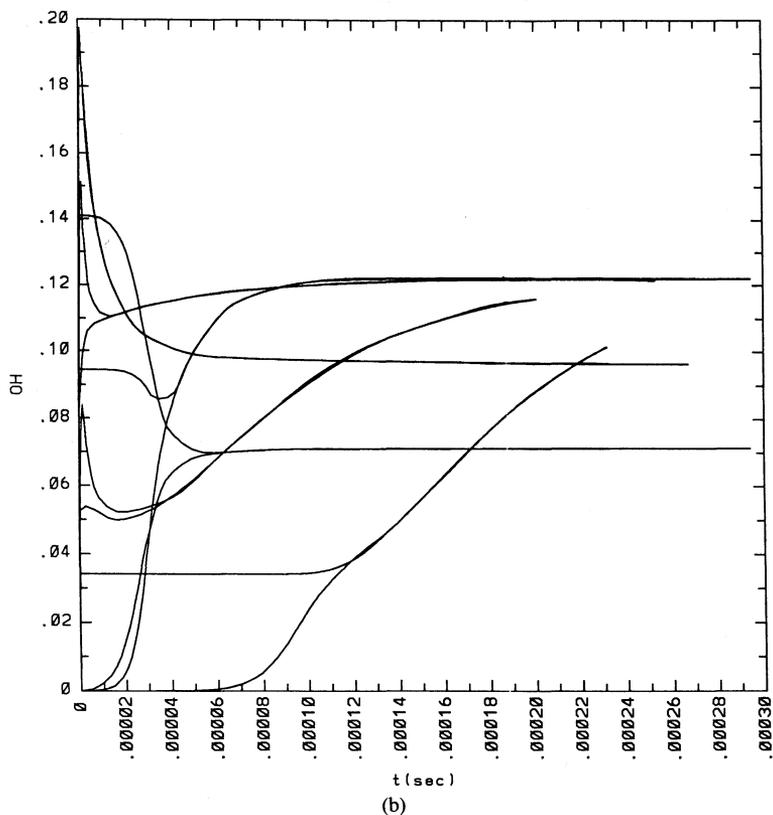
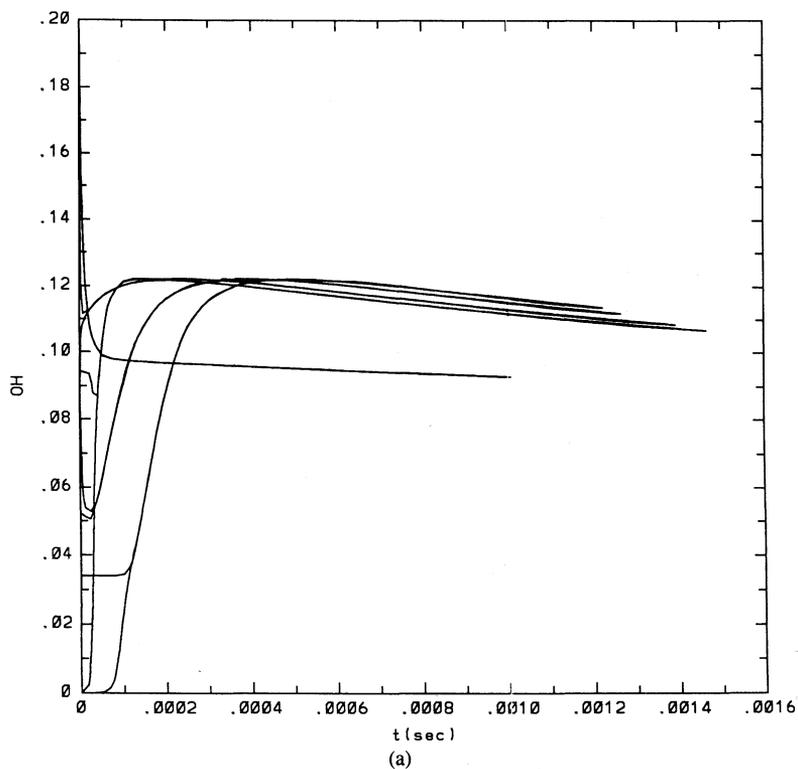


Fig. 10. (a) Plot of the specific mole number of H from sample trajectories and their projection on the manifold versus time. (b) Plot of the specific mole number of OH from sample trajectories and their projection on the manifold versus time.

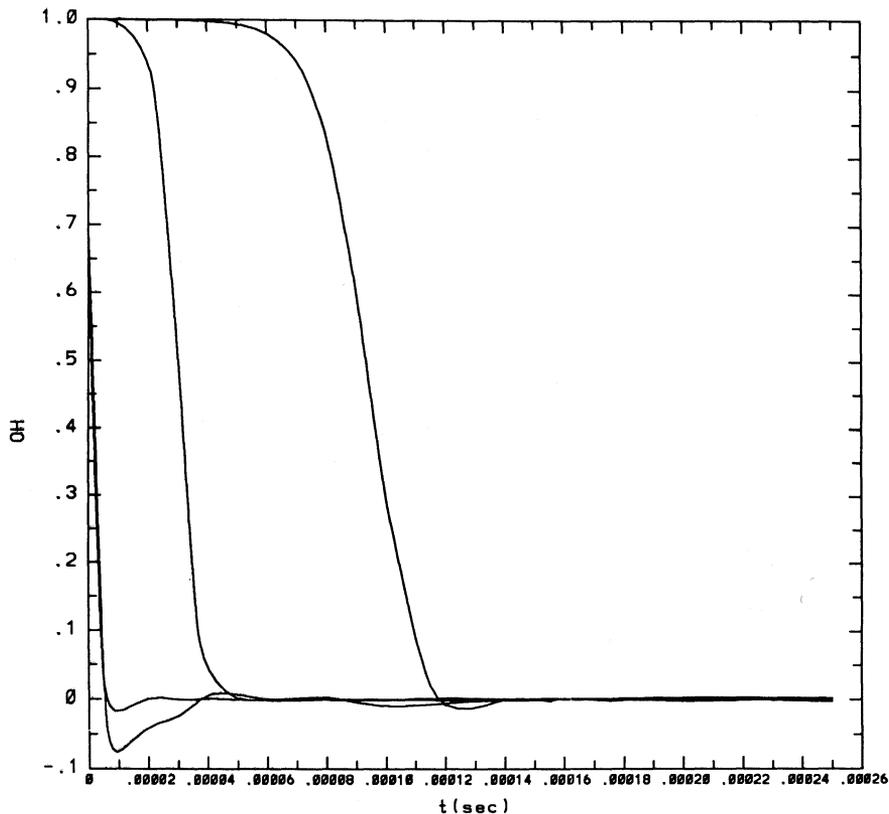


Fig. 11. Plot of the normed distance between sample trajectories and the manifold (see text).

order to tabulate the manifolds for subsequent use. This kind of representation of the results is not very convenient from a kineticist's viewpoint. As a consequence sensitivity results cannot be obtained directly. But our method is not aimed at obtaining kinetic details of a combustion system (here detailed numerical calculations of homogeneous ignition and one-dimensional laminar flames will very often provide the best insight). Our aim is to couple chemical kinetics with very complicated flow problems (like pdf methods for turbulent flows). In many of those models the computational effort forces a tabulation of the chemical kinetics in order to be able to treat not only idealized systems (like one-dimensional flames), but technically relevant three-dimensional processes in complex geometries. In principle all the method does is to uncouple fast time scales in the chemical kinetics and assume them to be in equilibrium. Thus, if one knows the "physical" time scales of the combustion process considered (e.g., diffusion, turbulent time scales), the method also allows one to decouple those fast chemical time scales that are much faster than the "physical"

time scales in systems other than homogeneous systems.

Although the methods of the approach discussed in this article are similar to those used by Lam and Goussis [11–13] (namely the dynamic systems theory), the aim and the realization of our approach is different in many aspects. Lam and Goussis use Computational Singular Perturbation for the analysis of distinct reaction trajectories. In their method they use refined basis vectors in order to decouple slow and fast time-scales. In this way they are able to integrate the stiff differential equation systems of chemical kinetics by means of explicit solvers with a very high accuracy [12]. At the same time (by identifying reaction groups) they obtain useful information about the chemical kinetics of the system. Our aim is quite different and motivated by the need of reduced schemes in turbulence modeling, especially in pdf methods. In those methods there is a high demand for reduced schemes that allow the treatment of complex reaction systems by a low-dimensional state space, that is, schemes that describe the reaction system in terms of only a

few state variables. Thus, in this case, it is necessary not to look at distinct trajectories in the reaction space, but to reduce the dimension of the state space globally. By means of the method of constructing intrinsic low-dimensional manifolds, we are able to describe the reaction space in terms of only a few parameters (i.e., controlling variables). Having determined such low-dimensional manifolds, it is possible to tabulate the results. In this way, for given values of the controlling variables, all the remaining state variables are explicitly given. The results then can be used to calculate the temporal development of the chemical states (by means of solving the chemical rate equations using detailed chemistry), which is used by a table-lookup, for example in pdf methods [15]. The computational cost for the calculation of the low-dimensional manifold and the integration of the corresponding rate equations are a small expense compared with the subsequent use in turbulence calculations.

The results presented in this article give only some examples of the potential of the method. Further work includes the implementation of the method in laminar and turbulent flame calculations, that is, the extension to nonhomogeneous problems [30]. One important question to be addressed is the choice of the parametrizing variables, which (as described above) does not influence the construction of the manifold, but only determines the way of mapping. Finally the numerical method that has been developed to determine the intrinsic manifold can be refined in several respects.

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## APPENDIX A: PARTIAL-EQUILIBRIUM AND STEADY-STATE ASSUMPTIONS

### Alternative Bases

The composition space  $\Phi$  is an  $n_s$ -dimensional space. The realizable subset is an  $(n_s - 1)$ -dimensional subspace (due to the constraint that the mass fractions sum to unity). In the composition space  $\Phi$  some distinct vectors have special meanings: a movement along a reaction vector  $\nu_i$  corresponds to a (possibly physically unrealistic) chemical reaction; a movement along an element vector  $\mu_i$  corresponds to a change of element composition (which is not allowed in chemical reactions). If we restrict to a given element composition, an  $(n_s - n_e)$ -dimensional linear subspace  $R$  of the composition space  $\Phi$  is defined, which contains all states that can be changed into another by chemical reaction. This subspace  $R$  shall be called the *reaction subspace*. It is spanned by reaction vectors  $\nu_i$ .

For further analysis it is useful to describe the state not in terms of specific mole numbers, but in terms of some other basis. Now, the composition space can be described in any convenient basis that spans the space [11]. For example, take a basis formed by  $n_s$  linearly independent vectors. The change of the basis is given by

$$Bs = \phi, \quad (A1)$$

where  $s$  are the new variables and  $B$  is the transformation matrix, with the column partitioning given by the basis vectors:

$$B = \begin{pmatrix} | & | & | & \cdots & | \\ \mathbf{b}_1 & \mathbf{b}_1 & \mathbf{b}_2 & \cdots & \mathbf{b}_{n_s} \\ | & | & | & & | \end{pmatrix}. \quad (A2)$$

The inverse of  $B$ ,  $B^{-1}$ , which is used for the transformation, is denoted by

$$B^{-1} = \begin{pmatrix} \text{---} & \tilde{\mathbf{b}}_1 & \text{---} \\ \text{---} & \tilde{\mathbf{b}}_2 & \text{---} \\ & \vdots & \\ \text{---} & \tilde{\mathbf{b}}_{n_s} & \text{---} \end{pmatrix}. \quad (A3)$$

The system of governing equations (Eq. 9) is transformed according to

$$\dot{s} = B^{-1}\Omega(s, h, P) = 0. \quad (A4)$$

(From now on, if an inverse of a matrix is formed, it shall always be assumed that the matrix is not singular.)

### Separation Into Conserved and "Reacting" Scalars

If  $B$  is a basis formed by  $n_e$  element composition vectors and  $n_r = n_s - n_e$  linearly independent reaction vectors, that is,

$$B = \begin{pmatrix} | & \cdots & | & | & \cdots & | \\ \mu_1 & \cdots & \mu_{n_e} & \nu_1 & \cdots & \nu_{n_r} \\ | & & | & | & & | \end{pmatrix}, \quad (A5)$$

the equation system is transformed to

$$\dot{s} = B^{-1}\Omega(h, P, s) = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ f_1 & (h, P, s) \\ \vdots \\ f_{n_r} & (h, P, s) \end{pmatrix}. \quad (A6)$$

Noting that the first  $n_e$  components of  $s$  are the coordinates  $\xi_i$  in the element space  $E$  (spanned by  $\mu_i$ ), while the remaining  $n_r$  components of  $s$  are coordinates  $r_i$  in the reaction space  $R$ ,

$$\begin{pmatrix} s_1 \\ \vdots \\ s_{n_e} \\ s_{n_e+1} \\ \vdots \\ s_{n_s} \end{pmatrix} = \begin{pmatrix} \xi_1 \\ \vdots \\ \xi_{n_e} \\ r_1 \\ \vdots \\ r_{n_r} \end{pmatrix}, \quad (A7)$$

the equation system reads

$$\begin{aligned} \dot{\xi} &= 0, \\ \dot{\mathbf{r}} &= \mathbf{f}(h, \mathbf{P}, \mathbf{s}). \end{aligned} \quad (\text{A8})$$

This means that in this basis we automatically separate into conserved and reactive variables, that is,  $n_e$  algebraic equations confine the chemical reaction to the reaction space,  $n_r$  differential equations describe the movement within the reaction space.

### Partial-Equilibrium Assumption

In partial-equilibrium schemes a set of (linearly independent) reactions is specified, which are assumed to have equal forward and reverse rates. To begin, for simplicity, we consider the partial-equilibrium assumption applied to reaction 1. By assumption, the forward and reverse rates of reaction 1 balance, and hence the reaction rate is zero:

$$f_1(h, \mathbf{P}, \mathbf{s}) = \tilde{\mathbf{b}}_{n_e+1} \boldsymbol{\Omega} = 0, \quad (\text{A9})$$

where  $\tilde{\mathbf{b}}_i$  is the  $i$ th row vector of the inverse  $B^{-1}$  of the transformation matrix. In the  $n_r$ -dimensional reaction space  $R$ , the points  $\mathbf{r}$  [recall  $\mathbf{s} = (\xi, \mathbf{r})$ ] that satisfy this nonlinear algebraic equation form an  $(n_r - 1)$ -dimensional nonlinear manifold,  $P_1$ . More generally if the first  $n_p$  reactions ( $n_p \leq n_r$ ) are in partial equilibrium, then the  $n_p$  equations  $f_i = 0$ ,  $i = 1, 2, \dots, n_p$  define an  $(n_r - n_p)$ -dimensional manifold  $P_{n_p}$  in  $R$ .

The idea behind the partial equilibrium assumption is that, except near  $P_{n_p}$ , the reaction rates  $f_i$ ,  $i = 1, 2, \dots, n_p$  are very large, causing the composition rapidly to approach the manifold  $P_{n_p}$ . This can be formalized by defining trajectories (from any initial composition) by the equations

$$\dot{\mathbf{r}} = \begin{pmatrix} \Lambda & f_1 \\ \Lambda & f_2 \\ & \vdots \\ \Lambda & f_{n_p} \\ & f_{n_p+1} \\ & \vdots \\ & f_{n_r} \end{pmatrix} \quad (\text{A10})$$

in the limit as  $\Lambda \rightarrow \infty$ . Thus, in the first infinitesimal time interval,  $r_{n_p+1}, r_{n_p+2}, \dots, r_{n_r}$  change infinitesimally, while  $r_1, r_2, \dots, r_{n_p}$  change to a point on the manifold  $P_{n_p}$ , so that  $\Lambda f_i$  is finite (i.e.,  $f_i = 0$ ,  $i = 1, 2, \dots, n_p$ ).

### Steady-State Assumption

In steady-state assumptions the time derivative of the concentrations of  $n_q$  distinct species is said to vanish, the species then obtaining steady states. Let the species be ordered so that the first  $n_q$  are in the steady state.

In this case the transformation matrix  $B$  is not only formed by the element and the reaction vectors, but also by the *species vectors*  $\sigma_i$ —the natural basis of the composition space:

$$\sigma_i = (\delta_{1,i}, \delta_{2,i}, \dots, \delta_{n_s,i})^T. \quad (\text{A11})$$

These are unit vectors that are orthogonal neither to the element, nor to the reaction vectors.

$$B = \begin{pmatrix} | & \cdots & | & | & \cdots & | & | & \cdots & | \\ \mu_1 & & \mu_{n_e} & \sigma_1 & & \sigma_{n_q} & \nu_1 & & \nu_{n_r} \\ | & & | & | & & | & | & & | \end{pmatrix} \quad (\text{A12})$$

The equations for the steady-state assumptions read

$$\tilde{\mathbf{b}}_{n_e+i} \boldsymbol{\Omega} = 0, \quad i = 1, 2, \dots, n_q, \quad (\text{A13})$$

where  $\tilde{\mathbf{b}}_i$  is the  $i$ th row vector of the inverse  $B^{-1}$  of the transformation matrix. Thus, if  $n_q$  species ( $n_q \leq n_r$ ) are assumed to be in steady state, then the  $n_q$  equations (A13) define an  $(n_r - n_q)$ -dimensional manifold  $Q_{n_q}$  in  $R$ .

### Combined Partial-Equilibrium and Steady-State Assumption

Of course quasi-steady-state and partial-equilibrium assumptions are usually combined. Thus the dimension of the reaction manifold (i.e., the subspace in which reaction proceeds) of a system with  $n_s$  species,  $n_e$  different elements,  $n_q$  quasi-steady-state and  $n_p$  partial equilibrium assumptions is given by  $n_m = n_s - n_e - n_p - n_q$ . As a result, if we have, for example, a one-step mechanism, this corresponds to a single line in

the reaction space, a two-step mechanism corresponds to a surface, and so on.

## APPENDIX B: RESPONSE OF A CHEMICAL SYSTEM TO DISTURBANCES

Let us start from the system equations of a reaction system, written in terms of element and reaction vectors. They are given by

$$\dot{s} = B^{-1}\Omega(h, P, s)$$

$$= F(h, P, s) = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ f_1(h, P, s) \\ \vdots \\ f_n(h, P, s) \end{pmatrix} \quad (\text{B1})$$

Now look at the behavior in the neighborhood of a point  $s^0$  in the composition space. Given that point, one may ask the following question: Suppose the state is perturbed to  $s^\epsilon$  (e.g., displaced by a certain error vector  $\epsilon$ ). How will the system respond? If we assume that the equations can be linearized in the neighborhood of  $s^0$ , the equations can be rewritten as

$$\frac{d}{dt}(s^\epsilon - s^0) = F_s(s^0, h, P)(s^\epsilon - s^0), \quad (\text{B2})$$

where  $F_s$  denotes the Jacobian  $\partial F/\partial s$ . With  $\epsilon = (s^\epsilon - s^0)$  the equation reads

$$\frac{d\epsilon}{dt} = F_s(s^0, h, P)\epsilon, \quad \epsilon(t=0) = \epsilon^0. \quad (\text{B3})$$

Suppose that the initial perturbation is given by  $\epsilon^0$ . Then  $\epsilon$  develops according to [20]

$$\epsilon(t) = e^{F_s t} \epsilon^0. \quad (\text{B4})$$

Now let us assume that  $F_s$  can be diagonalized. The finally presented method outlined in this paper, however is not based on this assumption. Now, if we define the perturbations in terms of the eigenvectors of the Jacobian ( $P\tilde{\epsilon} = \epsilon$ , with  $P$  as the modal matrix of the Jacobian), we finally end up with a very simple equation for the development of perturbations where the variables are

decoupled, namely:

$$\tilde{\epsilon}_i(t) = e^{\lambda_i t} \tilde{\epsilon}_i^0, \quad i = 1, 2, \dots, n_s, \quad (\text{B5})$$

where  $\lambda_i$  denote the eigenvalues of the Jacobian and  $\tilde{\epsilon}_i$  the components in the basis of the eigenvectors.

The significance of this equation system is: Suppose, that a chemical reaction system is perturbed in direction of the  $i$ th eigenvector of the Jacobian. Then there will be a response in the direction of this eigenvector, the time scale of the response given by the corresponding eigenvalue. There are three principal possibilities: (1)  $\lambda_i^r > 0$ , in which case the magnitude of the perturbation will increase; (2)  $\lambda_i^r = 0$ , in which case the magnitude of the perturbation will not change with time; and (3)  $\lambda_i^r < 0$ , in which case the magnitude of the perturbation will relax to zero. ( $\lambda_i^r$  denotes the real part of the eigenvalue.)

## APPENDIX C: BEHAVIOR OF A LINEARIZED SYSTEM

For an equation system

$$\frac{d\phi}{dt} = F(\phi), \quad \phi(t=0) = \phi^0, \quad (\text{C1})$$

the linearized equations in the neighborhood of  $\phi^0$  are given by

$$\frac{d}{dt}(\phi - \phi^0) = F(\phi^0) + F_\phi(\phi^0)(\phi - \phi^0) \quad (\text{C2})$$

Defining  $\varphi = \phi - \phi^0$ , the equation reads

$$\frac{d\varphi}{dt} = F(\phi^0) + F_\phi(\phi^0)\varphi. \quad (\text{C3})$$

If we assume for simplicity that the Jacobian  $F_\phi$  is not singular (in this case this corresponds, roughly speaking, to a system where all conserved variables have been eliminated), and making use of  $\varphi(t=0) = 0$ , the solution is simply given by

$$\varphi(t) = F_\phi^{-1}(e^{F_\phi t} - I)F(\phi^0). \quad (\text{C4})$$

Furthermore a change of the basis shall be introduced. If  $Q$  is defined as the matrix, whose column partition are the basis vectors, the variables  $\varphi$  are transformed into  $\psi$  according to  $Q\psi = \varphi$ , and the resulting equation system reads

$$\dot{\psi}(t) = Q^{-1}F_{\phi}^{-1}(e^{F_{\phi}t} - I)F(\phi^0). \quad (C5)$$

Performing straightforward operations on this equation, and using

$$Q^{-1}F(\phi^0) = \left. \frac{d\psi}{dt} \right|_{t=0} = \dot{\psi}(t=0), \quad (C6)$$

we end up with the equation system

$$\psi(t) = (e^{Nt} - I)N^{-1}\dot{\psi}(t=0), \quad (C7)$$

where  $N = Q^{-1}F_{\phi}Q$ . Thus the time development of the system can be expressed in terms of the rates  $d\psi/dt$  at  $t=0$ , that is, at the time when the system has the state  $\phi^0$ .

Now let us assume that we have chosen the transformation matrix  $Q$  such that  $N$  is an upper triangular matrix, with the eigenvalues appearing in the diagonal in decreasing order. (In fact such a transformation matrix always exists [21]). Then

the values of the  $\psi$  can be obtained recursively by

$$\begin{aligned} i &= n, n-1, \dots, 2, 1 \\ \psi_n &= a_{n,n}e^{b_{n,n}t}\dot{\psi}_n(t=0), \\ &\dots \dots \\ \psi_i &= \sum_{j=i}^n a_{i,j}e^{b_{i,j}t}\dot{\psi}_j(t=0), \\ &\dots \dots \\ \psi_1 &= \sum_{j=1}^n a_{1,j}e^{b_{1,j}t}\dot{\psi}_j(t=0), \end{aligned} \quad (C8)$$

where  $a$  and  $b$  are some coefficients that are not specified here. Immediately one can see the consequences for the system if, say, the last  $m$  rates  $\dot{\psi}_i$  equal zero at the point  $\phi^0$  in the composition space. Then we end up with an equation system where the  $\psi_i$  ( $i = n-m+1, \dots, n$ ) remain zero for all times (for the linear system). Thus, if the matrix  $N$  is chosen such that the eigenvalues of the Jacobian appear in descending order along the diagonal, this would mean that if we find all the states, where the initial rates  $\dot{\psi}_i$  for  $i = n-m+1, \dots, n$  are zero, we obtain the states from which reaction proceeds only according to slow time scales. Reactions with fast time scales would be in equilibrium in such systems.