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Simplification of Mathematical Models of Chemical Reaction Systems

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I. Introduction

Detailed modeling of complex reaction systems is becoming increasingly important in the development, analysis, design, and control of chemical reaction processes. For industrial processes, complete incorporation of the chemistry into process models facilitates the minimization of byproduct and pollutant formation, increased efficiency, and improved product quality. Processes that involve complex reaction networks include a variety of noncatalytic and homogeneous or heterogeneous catalytic processes (such as fluid catalytic cracking, combustion, chemical vapor deposition, and alkylation). For some systems, large sets of relevant reactions have been identified for use in simulations.[1-3] For others, the availability of advanced computing environments has enabled the automated generation of reaction networks and their models, based on computational descriptions of the reaction types occurring in the system.[4-6]

The use of such complex models is hindered by two obstacles. First, because of their sheer size and the presence of multiple time scales, these models are difficult to solve. Second, the models contain large numbers of uncertain (and sometimes unknown) kinetic parameters; regression to determine the parameters of complex nonlinear models is both difficult and unreliable, and the sensitivity of simulations to parameter uncertainties cannot be easily ascertained. Furthermore, for the purpose of gaining insights into the reaction system's behavior, it is usually preferable to obtain simpler models that bring out the key features and components of the system. For these reasons, model simplification and order reduction are becoming central problems in the study of complex reaction systems.

The simulation, monitoring, and control of a complex chemical process benefit from the derivation of accurate and reliable reduced models tailored to particular process modeling tasks. Model simplification is directly linked to identification of key reactions and sets of species that give valuable insights into the behavior of the network and how it may be influenced. Advanced control schemes such as model predictive control[7] or multiple model adaptive control[8] must be based on selecting appropriate reduced models and tracking key sets of species.

Ideally, a model order reduction algorithm should have broad applicability, enable analysis at several levels of detail, and provide an assessment of the modeling error.

II. Problem Formulation

The scope of this review will be confined to models of the dynamic behavior of reaction systems in which there are no explicit spatial variables. This includes well-mixed homogeneous processes, as well as those models of heterogeneous processes in which the spatial dependence has been neglected or already lumped. In general, a dynamic model of a reaction

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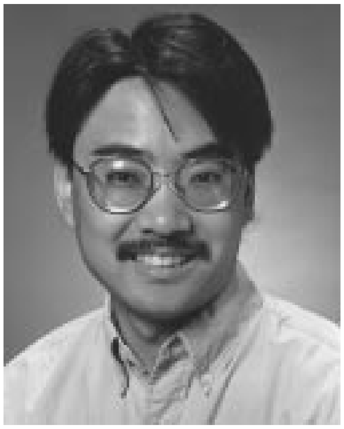

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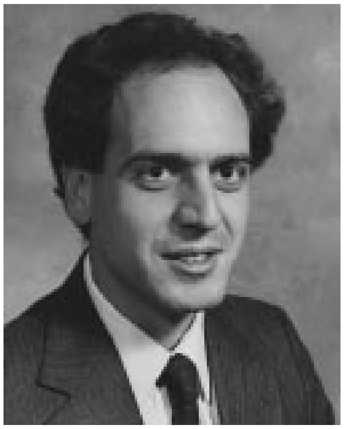

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network can be expressed as a set of ordinary differential equations[9]

$$\frac{d\mathbf{c}}{dt} = \mathbf{f}(\mathbf{c};\mathbf{k}), \quad \mathbf{c}(t_o) = \mathbf{c}_o \tag{1}$$

where $\mathbf{c}$ is the species concentration vector (dimension n), $\mathbf{k}$ is the vector of reaction rate constants, and $\mathbf{f}$ is the vector of operators expressing the kinetics. Recent work has shown the possibility of describing chemical reaction systems through other kinds of equations, such as delay differential equations;[10] these nontraditional modeling schemes can only be applied to limited types of systems and will not be reviewed here.

In the context of chemical reaction systems, *model order reduction* refers to the identification of relationships among the reactants, so that fewer species need to be independently tracked (simulated or measured). The goal of model order reduction is to transform the system of differential equations (1) to one of lower order and still retain the key dynamic information. The reduced system is

$$\frac{d\hat{\mathbf{c}}}{dt} = \hat{\mathbf{f}}(\hat{\mathbf{c}};\hat{\mathbf{k}}), \quad \hat{\mathbf{c}}(t_o) = \hat{\mathbf{c}}_o \tag{2}$$

where $\hat{\mathbf{c}}$ is the species vector in the reduced model (dimension $\hat{n} < n$), $\hat{\mathbf{k}}$ is the vector of rate constants in the reduced system, and $\hat{\mathbf{f}}$ is the resulting kinetics vector. Note that $\hat{\mathbf{c}}$ may refer to a subset of the original species, to groups of original species, or to linear combinations and other mathematical constructs (in effect defining new variables rather than just a selected subset of the original variables). The neglected individual concentrations may be combined with other species, replaced by algebraic relations, or ignored completely. The reduced system (eq 2) should be more tractable mathematically and computationally, give greater insight into the key relationships among species, and contain fewer unknown parameters than the full model (eq 1).

Three general strategies have been pursued for model order reduction: lumping, sensitivity analysis, and time-scale analysis. *Lumping* transforms the original variables to a lower dimensional vector (Figure 1a):

$$\hat{\mathbf{c}} = \mathbf{h}(\mathbf{c}) \tag{3}$$

The transformation may be based on some set of physical properties or on the reactivity of the compounds. Lumping is useful when only limited measurements and information are available about specific reaction kinetics and detailed chemical composition. In a lumped model, information about specific reactions and species is often concealed. *Sensitivity analysis* seeks to determine and eliminate insignificant reactions and species on the basis of their impact on designated important species; only a subset of the original species remain in the reduced model (Figure 1b). As the number of important species increases, sensitivity analysis is less likely to provide substantial model order reduction. For this reason, sensitivity analysis is often used in conjunction with the quasi-steady-state approximation. *Time-scale analysis* identifies the different scales over which species react, and the fast-time-scale reactions and species are assumed to be at steady state. The slow variables, $\hat{\mathbf{c}}$, remain in the reduced model, yet their motion is constrained to a lower dimensional space on the basis of their relationship to the fast variables, $\mathbf{c}_f$ (Figure 1c):

$$\mathbf{c}_f = \mathbf{g}(\hat{\mathbf{c}}) \tag{4}$$

Thus, order reduction is possible as the differential equations for the fast species are replaced by algebraic relations. This is the basis for the quasi-steady-

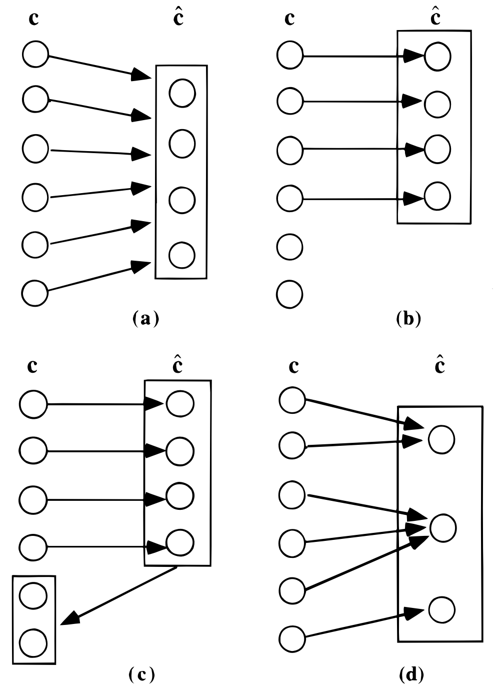


Figure 1. Schematic representations of model reduction techniques. (a) Lumping transforms the species vector to one of lower dimension, $\hat{\mathbf{c}} = \mathbf{h}(\mathbf{c})$. (b) Sensitivity analysis neglects species whose impact is small. (c) In time-scale analysis, fast species are derived from algebraic constraints, $\mathbf{c}_f = \mathbf{g}(\hat{\mathbf{c}})$. (d) Linear proper lumping is a special case of (a) where species form independent pools. Mathematically, the transformation is $\hat{\mathbf{c}} = \mathbf{M}\mathbf{c}$, where M_{ij} is equal to 1 when c_j contributes to $\hat{\mathbf{c}}_i$ and 0 otherwise.

state approximation, which has been mathematically formalized by singular perturbation theory. Time-scale analysis requires manual manipulation of the model and significant a priori knowledge of the behavior of various species; in practice, this means that it is feasible to simplify only compact models.

III. Lumping

Lumping is a widely used method for simplifying reaction kinetics. The reactant vector is transformed to a lower dimensional vector of pseudospecies so that the kinetic equations are easier to solve, and fewer parameters need to be experimentally determined. The most accessible lumping schemes are linear, as suitable nonlinear transformations are difficult to determine. Mathematically, linear lumping falls into two categories, proper and improper. In *proper lumping* (Figure 1d), each reactant appears in only one lump, so that each lump follows the *principle of invariant response*:[11] the rate of reaction of the lump should depend only on the sum of the species and not on the individual species it contains. Empirically determined lumps are nearly always proper. In *improper lumping*, on the other hand, components may contribute to more than one lump. Proper lumping schemes are more insightful and useful, but for realistic reaction networks many mathematical lumping methods are able to derive only improper lumps.

The use of lumped models was reported as early as 1953,[12] with the reduced scheme being empirically determined. Mathematically rigorous lumping techniques create lumps that are an integral of a set defined by a continuous index variable (continuum view[13]), or functions of the individual chemical species (discrete view[11]). Continuum lumping is linear and proper, while both linear and nonlinear techniques have been presented for the determination of discrete lumps. The applicability of each method depends on the structure of the system as well as the extent of available information on kinetics and composition.

A. Lumping a Continuum

The treatment of a complex mixture as a continuum was first proposed by DeDonder.[14] As the number of species in a mixture approaches infinity, it is no longer possible to identify specific individual species, but only a distribution of species. Such a view is convenient when the exact composition and reactions are unknown, since the continuous view does not provide a direct way to incorporate known detailed kinetic information. If all the reactants are combined into a single, proper lump, only the disappearance of that lump is tracked in the reduced model.[13,15−17]

A continuous mixture can be described in terms of the rate constants, $\mathbf{k}$, or physical properties such as boiling point, molecular weight, or molecular structure.[18] However, it is advantageous to define the mixture in terms of a nondimensional indexing variable.[19,20] The index variable, x, is taken to be in the interval $[0,\infty)$. The initial concentration of material specified over the interval $(x,x+\mathrm{d}x)$ is given as

$$c(x,0)\,\mathrm{d}x = c_0 h(x)\,\mathrm{d}x \tag{5}$$

where c_0 is the total initial concentration, and $h(x)$ is a distribution function. The distribution function $h(x)$ must be normalized so that

$$\int_0^\infty x h(x)\,\mathrm{d}x = 1 \tag{6}$$

and the mathematical treatment is simplified without loss of generality by scaling the index variable so that

$$\int_0^\infty x h(x)\,\mathrm{d}x = 1 \tag{7}$$

For a first-order irreversible reaction, the model takes the form

$$\frac{\mathrm{d}}{\mathrm{d}t} c(x,t) = -k(x)\,c(x,t) \tag{8}$$

The index variable is defined so that the rate constants are ordered. Then, $k(x)$ is a monotonically increasing function on $[0,\infty)$, with $k(0) = 0$ and $k(x) \to \infty$ as $x \to \infty$. The solution of eq 8 gives the concentration over an interval to be

$$c(x,t) = c_0 h(x)\,\mathrm{e}^{-k(x)t} \tag{9}$$

Integrating over the index variable then yields an expression for the entire lump, C

$$C(t) = \int_0^\infty [c(x,t)\,\mathrm{d}x]/c_o = \int_0^\infty h(x)\,\mathrm{e}^{-k(x)t}\,\mathrm{d}x \qquad (10)$$

and its time derivative

$$\dot{C}(t) = -\int_0^\infty k(x)\,h(x)\,\mathrm{e}^{-k(x)t}\,\mathrm{d}x = -F(C) \qquad C(0) = 1 \qquad (11)$$

One possible function for $h(x)$ is the Γ distribution,[15]

$$h(x) = [\alpha^\alpha x^{\alpha-1}/\Gamma(\alpha)]\mathrm{e}^{-\alpha x} \qquad (12)$$

where $\alpha > 0$ is a characteristic parameter of the system. Through the use of the Laplace transform on $h(x)$, the functional dependence of the decay of the lump is found to be

$$F = \hat{k}C^n \qquad (13)$$

where $\hat{k}$ is an average rate constant

$$\hat{k} = \int_0^\infty k(x)\,h(x)\,\mathrm{d}x \qquad (14)$$

and n is the apparent reaction order, related to the parameter α by

$$n = 1 + 1/\alpha \qquad (15)$$

The kinetic behavior of the lump is then given by the solution of eq 11

$$C = \{1 + (n-1)\hat{k}t\}^{-1/(n-1)} \qquad (16)$$

where the apparent reaction order is $n \geq 1$.

This approach provides a solid theoretical basis for continuous lumping of mixtures whose individual components decay by first-order, irreversible, parallel reactions. In applications, experimental data must exist to fit the apparent reaction order n (eq 16) and in most cases $\hat{k}$, because for a complex mixture it is unlikely that the function $k(x)$ (eq 14) will be known.

Many processes of interest, especially in catalysis, are known to have nonlinear intrinsic kinetics. The above approach does not extend directly to higher order systems,[21] as this results in a physically invalid model which violates the single-component identity (SCI). The SCI states that if all components have the same value for their kinetic parameters, a valid lumped model must reduce to the kinetics of a single component.

Researchers have taken two approaches to retain the physical validity of lumped models for systems with nonlinear kinetics. Astarita and Ocone initiated a solution through the use of cooperative kinetics,[20] while Chou and Ho used a coordinate transformation[22] to obtain a solution.

The cooperative kinetics approach seeks to linearize the system through the use of the *warped time* concept.[16,23] The key assumption is that the nonlinear kinetics differ from the linear case by a factor that has the same value for each component in the mixture. With the addition of an interaction function, $K(x,z)$, the model is written similarly to eq 8 as

$$\frac{\mathrm{d}}{\mathrm{d}t}c(x,t) = -k(x)\,c(x,t)\,F[\int_0^\infty K(x,z)\,c(z,t)\,\mathrm{d}z] \qquad (17)$$

The function $K(x,z)$ represents the effect of the z-index component on the kinetics of the x-index component. Thus, the total effect of all other components on the x-index component is the integral of $K(x,z)$ weighted by the concentration $c(z,t)$. The key assumption of cooperative kinetics requires $K(x,z)$ to be a function of z only:

$$\frac{\mathrm{d}}{\mathrm{d}t}c(x,t) = -k(x)\,c(x,t)\,F[\int_0^\infty K(z)\,c(z,t)\,\mathrm{d}z] \qquad (18)$$

Thus, the system is linearized, and a solution for $c(x,t)$ is found which is similar to eq 9:

$$c(x,t) = c(x,0)\,\mathrm{e}^{-k(x)w(t)} \qquad (19)$$

The additional function, $w(t)$, is known as the warped time, and can be found by solving a separate ordinary differential equation:

$$\frac{\mathrm{d}w}{\mathrm{d}t} = F[\int_0^\infty K(z)\,c(z,0)\,\exp(-k(z)\,w(t))\,\mathrm{d}z] \qquad w(0) = 0 \qquad (20)$$

Equation 19 may then be used in the development of a continuous lumping scheme as described previously. The assumptions of cooperative kinetics are restrictive, but they are applicable to many types of chemical systems: catalytic reactions governed by Langmuir isotherm adsorption,[16,20] and more generally under the assumption of uniform catalytic surface coverage,[15] Michaelis Menten kinetics for enzymatic reactions,[24] and biomolecular reactions under the assumption of intrinsic reactivity.[16] This approach has also been shown to be applicable in adiabatic systems, where the nonlinearity is introduced by temperature variations.[16]

Another approach for continuous lumping of reactions with intrinsic nonlinear kinetics is through a coordinate transformation.[22] This method approximates the finite sum of reactants with respect to a discrete indexing variable, i, as an integral over the reactivity k. The Jacobian of this i-to-k transformation, $D(k_i)$, can be used to define the reactant concentration over an interval Δi to be

$$c_i(t) = c(k_i,t)\,D(k_i)\,\Delta k_i \qquad (21)$$

The total reactant lump can then be approximated by a weighted integral:

$$C(t) = \int_0^\infty c(k,t)\,D(k)\,\mathrm{d}k \qquad (22)$$

In systems so complex as to warrant a continuous description, the function D is likely to be undetermined. Thus, these models are practical for studying only the long time behavior of a lump by extending an asymptotic analysis[25] to these transformed systems. For irreversible reactions with nonlinear kinetics, the concentration of reactant k can be described as

$$c(k,t) = c(k,0)[1 + (n-1)c(k,0)^{n-1}kt]^{1/(1-n)} \qquad (23)$$

Then substituting eq 23 in eq 22, for $n \geq 1$, the concentration lump can be described as

$$C(t) = \int_0^\infty c(k,0)\, D(k)\, [1 + (n-1)c(k,0)^{n-1}kt]^{1/(1-n)}\, \mathrm{d}k \quad (24)$$

At long times, the integrand is significant in a thin region near $k = 0$ so eq 24 can be simplified to

$$C(t) = c(0,0)\, D(0) \int_0^\infty [1 + (n-1)c(0,0)^{n-1}kt]^{1/(1-n)}\, \mathrm{d}k \quad (25)$$

and solved analytically for $1 \leq n < 2$

$$C(t) = \frac{1}{t}\left\{\frac{c(0,0)^{2-n}\, D(0)}{2-n}\right\} \quad (26)$$

For $n \geq 2$, a numerical solution is possible if the forms of $D(k)$ and $c(k,0)$ are known.

The continuum lumping methods described in this section cannot be used for mixtures that are too complex to characterize by only one indexing variable. To account for and track the complexity of a mixture, Prasad et al. proposed using two indices to create continuous lumps.[26] Each indexing function can then track a separate physical parameter. For example, in the analysis of coal liquefaction, both carbon number and oxygen atoms need to be tracked to produce a useful lumped model.

A drawback of continuum lumping is that the method does not provide a convenient way to incorporate known information about the specific reactants or reactions; it relies instead on empirically fitted parameters. Despite the limitations of the continuum description, it is finding use because of the agreement with coarse experimental observations, the tractability of the mathematical treatment, the compactness of the solution, and the applicability to poorly defined systems. The total concentration of a complex reactant mixture where each individual component reacts by a first-order reaction, as is the case in petroleum cracking, is observed to decay by a higher order of reaction,[15,27] as predicted by Krambeck.[25] Continuum lumps have been exploited in the modeling of petroleum cracking,[17,24,27] incorporated into reactor models,[28] and used for diffusion−reaction systems.[29]

B. Discrete Lumping

Discrete lumping[11,30−32] treats the components in a complex mixture individually, and transforms them on the basis of their reactivity. Linear lumping methods may result in either proper or improper lumping schemes, depending on the reaction kinetics. In theory, nonlinear methods are more widely applicable, but the requisite transformations can generally be found only for reaction systems where the relative time scales of the species are known. The discrete approach requires a comprehensive description of the kinetic scheme. This information may be the actual species and reactions, but it is also possible to use discrete lumping to further simplify a system of empirical lumps.

Discrete linear lumping transforms the species vector to one of lower dimension through matrix operations. For a system of unimolecular reactions, eq 1 becomes

$$\frac{\mathrm{d}\mathbf{c}}{\mathrm{d}t} = -\mathbf{K}\mathbf{c} \quad (27)$$

where $\mathbf{c}$ is a vector of dimension n and $\mathbf{K}$ is a square matrix of the rate constants. The diagonal elements of $\mathbf{K}$, k_{ii}, represent the sum of rate constants corresponding to the total consumption of species i, while the off-diagonal elements, k_{ij}, represent the rate constants of the conversion of species j to species i. To reduce the order of the system, lumps are constructed as

$$\hat{\mathbf{c}} = \mathbf{M}\mathbf{c} \quad (28)$$

where $\hat{\mathbf{c}}$ is of dimension $\hat{n} < n$ and $\mathbf{M}$ is the lumping matrix of dimension $\hat{n} \times n$. This system is exactly lumpable if there exists a matrix $\hat{\mathbf{K}}$ such that the kinetic behavior of the lumped system can be described by

$$\frac{\mathrm{d}\hat{\mathbf{c}}}{\mathrm{d}t} = -\hat{\mathbf{K}}\hat{\mathbf{c}} \quad (29)$$

By recognizing that eq 29 may be obtained by either substituting the lumps into the kinetic scheme or lumping the kinetic scheme, Wei and Kuo[11] determined a necessary and sufficient condition for exact lumping of linear systems to be

$$\mathbf{MK} = \hat{\mathbf{K}}\mathbf{M} \quad (30)$$

Equation 30 will always be satisfied if the left $\hat{n}$ eigenvectors of the reactivity matrix, $\mathbf{K}$, are chosen to compose $\mathbf{M}$, and $\hat{\mathbf{K}}$ is a diagonal matrix with the corresponding eigenvalues of $\mathbf{K}$. Order reduction is evident when the matrix of eigenvectors, $\mathbf{X}$, is considered as

$$\mathbf{MX} = \hat{\mathbf{X}}(\hat{\mathbf{I}}|\mathbf{0}) \quad (31)$$

The nonsingular matrix of lumped eigenvectors is $\hat{\mathbf{X}}$ $(\hat{n} \times \hat{n})$, while $(\hat{\mathbf{I}}|\mathbf{0})$ is a matrix whose left submatrix $\hat{\mathbf{I}}$ is an $\hat{n} \times \hat{n}$ identity matrix and right submatrix $\mathbf{0}$ is an $\hat{n} \times (n - \hat{n})$ null matrix. Thus, the lumping matrix $\mathbf{M}$ reduces the dimensionality of the system and eliminates $(n - \hat{n})$ of the eigenvectors of the reactivity matrix.

For linear systems, there are an infinite number of exact lumping schemes, although not all will be proper. As proper lumps are more insightful and useful, many systems may be approximately reduced into proper lumps.[33] The error matrix

$$\mathbf{E} \equiv \mathbf{MK} - \hat{\mathbf{K}}\mathbf{M} \quad (32)$$

reflects the accuracy of a given approximate proper lumping scheme.

The above analysis provides a theoretical basis for discrete lumping methods. For a system of unimolecular reactions, it provides the necessary and sufficient conditions for exact lumping and guidelines for the applicability of approximate lumping.

Other developments in lumping address more practical issues and diverse reaction systems. Coxson and Bischoff examined the construction of proper lumps from response data.[30] The data from a unimolecular reaction system are analyzed at discrete times, and the response vectors are examined to determine which may be combined on the basis of the principle of invariant response. For small systems, this can be done by inspection, while for other systems the statistical method of clustering analysis is utilized. However, for very large systems, the results from clustering analysis are difficult to interpret. Coxson and Bischoff suggest starting the method from the minimum number of empirical lumps that still preserve the desired accuracy, and then applying clustering analysis to further reduce the number of these lumps. In this manner, a petroleum cracking model was reduced from ten lumps[34] to a unimolecular system of six lumps.

Two key elements are required to achieve wide applicability for discrete lumping: extensions to nonlinear reaction systems, and methods for identifying lumping schemes a priori (before obtaining experimental concentration profiles). An initial extension of the work of Wei and Kuo to bimolecular systems was performed by Li;[35] subsequently Li and Rabitz generalized the analysis of discrete lumping to systems with arbitrary nonlinearities through the use of invariant subspaces of the reaction system.[36] The exactly lumped system of equations would be

$$\frac{\mathrm{d}\hat{\mathbf{c}}}{\mathrm{d}t} = \mathbf{M}\mathbf{f}(\bar{\mathbf{M}}\hat{\mathbf{c}}) \qquad (33)$$

where $\bar{\mathbf{M}}$ is a generalized inverse of $\mathbf{M}$ satisfying

$$\mathbf{M}\bar{\mathbf{M}} = \mathbf{I}_{\hat{n}} \qquad (34)$$

The necessary and sufficient condition for exact lumping of a nonlinear system is that the transpose of the Jacobian matrix, $\mathbf{J}^{\mathrm{T}}(\mathbf{c})$, of $\mathbf{f}(\mathbf{c})$ has nontrivial fixed invariant subspaces M. The basis vectors of M construct the lumping matrix $\mathbf{M}$. An appropriate lumping matrix is found by minimizing the error, $Z(\mathbf{c})$, of such a lumping scheme

$$Z(\mathbf{c}) = tr[E^{\mathrm{T}}(\mathbf{c})\, E(\mathbf{c})] \qquad (35)$$

where

$$E(\mathbf{c}) = (I_n - \mathbf{M}^{\mathrm{T}}\mathbf{M})\mathbf{J}^{\mathrm{T}}(\mathbf{c})\mathbf{M}^{\mathrm{T}} \qquad (36)$$

and tr is the trace of a matrix (the sum of the eigenvalues, also equal to the sum of the diagonal elements).

The nonlinear system is analyzed through its instantaneous linearized versions. The Jacobian is decomposed as follows

$$\mathbf{J}^{\mathrm{T}}(\mathbf{c}) = \mathbf{A}_{\mathrm{o}} + \sum_{k=1}^{m} a_k(\mathbf{c})\mathbf{A}_k \qquad (37)$$

The $a_k(\mathbf{c})$ coefficients are functions of $\mathbf{c}$, and the $\mathbf{A}_k$ matrixes are constant and form a basis of $\mathbf{J}^{\mathrm{T}}(\mathbf{c})$. A subspace that is simultaneously invariant for all the $\mathbf{A}_k$ matrixes is also a fixed invariant subspace of $\mathbf{J}^{\mathrm{T}}(\mathbf{c})$. Note that, although the kinetics are nonlinear, the species transformation (eq 28) is linear. The decomposition (eq 37) of the Jacobian also involves a linear expression, but with potential nonlinear functions of the concentration $a_k(\mathbf{c})$. The optimization problem to find $\mathbf{M}$ then becomes

$$\min Z(\mathbf{c}) = tr\sum_{k=1}^{m} \mathbf{M}\mathbf{A}_k{}^{\mathrm{T}}(\mathbf{I}_n - \mathbf{M}^{\mathrm{T}}\mathbf{M})\mathbf{A}_k\mathbf{M}^{\mathrm{T}}$$
$$\text{subject to} \quad \mathbf{M}\mathbf{M}^{\mathrm{T}} = \mathbf{I}_{\hat{n}} \qquad (38)$$

For unconstrained lumping, the initial guess is based on an $\mathbf{M}$ which defines a subspace that has a high degree of coincidence with the invariant subspaces of the $\mathbf{A}_k$ matrixes.[37]

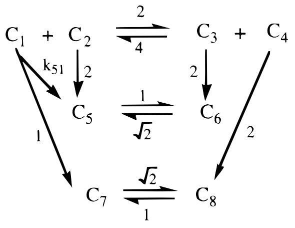
This method lends itself to constrained lumping techniques,[37] where components of interest can be left unlumped. The lumping matrix, $\mathbf{M}$, becomes

$$\mathbf{M} = \begin{pmatrix} \mathbf{M}_{\mathrm{G}} \\ \mathbf{M}_{\mathrm{D}} \end{pmatrix} \qquad (39)$$

where $\mathbf{M}_{\mathrm{G}}$ is given by the modeler and $\mathbf{M}_{\mathrm{D}}$ is determined from a search of the invariant subspaces of the system. The matrix $\mathbf{M}_{\mathrm{G}}$ is useful to separate species which must be tracked during the reaction. This added constraint also facilitates the search for appropriate lumping schemes,[31] but may increase the error for a desired model order.

A major accomplishment was the determination of a lumping scheme a priori for exactly lumpable systems,[36] and possible approximate lumping schemes for isothermal nonlinear systems.[31,37] The method has also provided the foundation for lumping nonisothermal first-order reaction systems.[38]

An illustration of approximate linear lumping has been shown with the following example system:[31]



This reaction system is exactly lumpable when $k_{51} = 1$.[36] In this example, k_{51} is set to 0.1 so that the lumping schemes will be approximate. Also, the concentrations of c_1, c_2, c_3, and c_4 were separated into a constrained lump, $\hat{c}_1$. Thus, the composition of $\hat{c}_1$ will remain the same for each lumping scheme. The results of the reduced models are shown in Figure 2. For this system, only the 2-dimensional lump shows significant deviation from the full model.

The use of invariant subspaces for determining an approximate lumping scheme first seeks out the lowest order reduced model; then, to increase accuracy, lower order schemes are used as starting points in seeking higher order lumping schemes. This method of searching for lumping matrixes is disadvantageous for strongly coupled systems with multiple time scales, and suitable fixed invariant subspaces of the transpose of the Jacobian may not exist for many nonlinear systems.

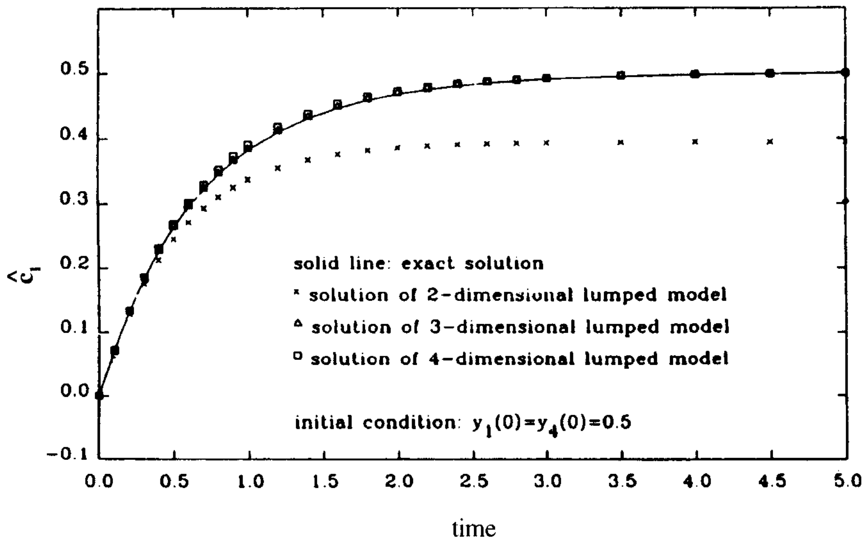


Figure 2. Comparison of the lumped model to the full simulation. Reprinted with permission from ref 31. Copyright 1991 Elsevier Science Ltd.

Progress in developing lumped models may lie in inherently nonlinear lumping techniques[39] and the direct incorporation of time-scale separation techniques in lumping.[40,41] These methods are closely related as both seek to find an expression for the invariant manifold that exists in state space for a given transformation. In nonlinear lumping, the concentrations are transformed by

$$\hat{\mathbf{c}} = \mathbf{h}(\mathbf{c}) \tag{40}$$

where **h** is the lumping transformation operator. The reaction system (eq 1) then becomes

$$\frac{d\hat{\mathbf{c}}}{dt} = \mathbf{h}_c[\bar{\mathbf{h}}(\hat{\mathbf{c}})]\ \mathbf{f}[(\bar{\mathbf{h}}(\hat{\mathbf{c}})] \tag{41}$$

where $\mathbf{h}_c(\mathbf{c})$ is the Jacobian matrix of $\mathbf{h}(\mathbf{c})$ and $\bar{\mathbf{h}}$ is the generalized inverse of **h** satisfying

$$\mathbf{h}(\bar{\mathbf{h}}) = \mathbf{I}_{\hat{n}} \tag{42}$$

The difficulty in nonlinear lumping is the absence of a general reliable method to determine the transformation **h** and its inverse $\bar{\mathbf{h}}$. However, nonlinear lumping schemes can be determined when a reaction system (eq 1) can be separated along time scales into the form[42]

$$\frac{d\mathbf{y}}{d\tau} = \mathbf{f}^1(\mathbf{y},\mathbf{z};\mathbf{k}) + \epsilon\mathbf{f}^2(\mathbf{y},\mathbf{z};\mathbf{k}) \tag{43}$$

$$\frac{d\mathbf{z}}{d\tau} = \mathbf{g}^1(\mathbf{y},\mathbf{z};\mathbf{k}) + \epsilon\mathbf{g}^2(\mathbf{y},\mathbf{z};\mathbf{k}) \tag{44}$$

where **y** and **z** are vectors of concentrations reacting along the slow and fast time scales, respectively, **f** and **g** are operator vectors, ϵ is a small parameter from the ratio of time scales, and τ is the fast time variable

$$\tau = t/\epsilon \tag{45}$$

The determination of approximate nonlinear lumping schemes is possible because the differential operator

$$A = \sum_{i=1}^{n} f_i(\mathbf{c}) \frac{\partial}{\partial c_i} \tag{46}$$

for the original reaction system (eq 1)

$$\frac{dc_i}{dt} = f_i(\mathbf{c}) = Ac_i \qquad i = 1, ..., n \tag{47}$$

can be expressed as a series containing the small perturbation parameter. An algebraic method for transformingto a canonical form has been pre-

$$A = A_0 + \epsilon A_1 + \epsilon^2 A_2 + ... \tag{48}$$

sented.[43] The transformation defines a new basis consisting of the invariants and eigenfunctions of A_0, leading to a differential equation system which contains only the slow variables. The slow variables are invariants of A_0 and can be decoupled from the fast variables, which are then lumped in the eigenfunctions so that the new starting basis takes the form

$$\{\phi_1(\mathbf{y},\mathbf{z}),\phi_2(\mathbf{y},\mathbf{z}),...,\phi_m(\mathbf{y},\mathbf{z}),y_1,y_2,...,y_{\hat{n}}\} \tag{49}$$

The operator expressing the lumped model, M, is found by defining a transformation operator, S, such that

$$M = e^{-S} A e^{S} \tag{50}$$

Then S is expressed as a series

$$S = \epsilon S_1 + \epsilon^2 S_2 + ... \tag{51}$$

so that M is of the same canonical form as A_0. Such a transformation effectively decouples the slow variables from the fast variables, so that a reduced order system can be written in terms of only the slow variables

$$\frac{d\hat{\mathbf{y}}}{dt} = \hat{\mathbf{f}}(\hat{\mathbf{y}};\mathbf{k},\epsilon) \tag{52}$$

where

$$\hat{y}_i = e^{S} y_i \tag{53}$$

The solution of the original variables can be found from the inverse transformation

$$y_i = e^{-S} \hat{y}_i \tag{54}$$

and if some of the slow variables need to remain unchanged, a constraint may be placed on the transformation operator[44]

$$S y_i = 0 \tag{55}$$

The system of fast variables

$$\frac{d\hat{\phi}}{dt} = \hat{\mathbf{g}}(\hat{\mathbf{y}},\hat{\phi};\mathbf{k},\epsilon) \tag{56}$$

where $\phi_{\hat{i}}$ is defined in the same manner as $\hat{y}_i$ (eq 53), can then be evaluated separately. This form is useful in solving for the evolution of the fast variables in the boundary layer by setting $\hat{\mathbf{y}} = \hat{\mathbf{y}}(0)$ or for getting values for the fast variables as functions of time.

This nonlinear method requires that the relative scales in a reaction system be known a priori, as it depends on the proper introduction of ϵ. The zero-order approximation of constrained nonlinear lumping for the reduced system is equivalent to the well-known quasi-steady-state approximation (to be discussed later in this review), while the higher order terms result in increased accuracy over a larger region. This method was used to generate reduced models for an enzyme-catalyzed reaction[42] and a compact subset of hydrogen combustion.[44] The method works well for compact systems, yet the higher order terms of M become increasingly difficult to compute as the systems become larger.

A common feature of lumping techniques is the loss of information about specific components and individual reactions. In some cases, this is an advantage since unknown kinetic constants and species are lumped together so that fewer parameters need to be determined. This assumes that the sets of species that are mathematically convenient to lump also happen to be the ones that do not need to be resolved for the process modeling objective at hand.

An approach for including known reaction types into a proper empirical scheme is to assume a representative distribution of components within the lumps. Reduced models for catalytic cracking have been constructed by assigning a single representative structure per carbon number per compound class lump.[32,45] A similar approach has also been applied to oxidation systems[46,47] where a specific radical species was chosen to represent a class of intermediates. This approach enables the incorporation of known kinetic data, although specific components are not tracked. Clearly, the success of such an approach depends on how similarly the compounds behave and how well the representatives are chosen.

Lumping is a widely used model simplification technique and has shown success with several reaction systems. However, the inherent loss of information about individual species and reactions and resulting lower accuracy are significant obstacles in its application. Furthermore, the difficulty in finding appropriate lumping schemes increases dramatically for large nonlinear reaction networks.

IV. Sensitivity Analysis

Sensitivity analysis has been used to analyze chemical[48,49] and biological[50] systems, primarily to examine their behavior with respect to disturbances or to determine the robustness of parameter estimation. The extension to model reduction lies in the fact that a particular process modeling objective rarely depends on every single component in a complex reaction system. Therefore, a satisfactory description of the system need only include the *important species*, which are relevant for the task at hand, and the *necessary species*, which have a significant effect on the important species. Thus, by removing the species that have only a weak influence on important and necessary species, the order of the system is reduced.[51−54]

Turanyi et al. discussed how sensitivity analysis may be used to reduce the complexity of a kinetic model systematically.[51] The procedure entails (1) identifying the important species, (2) determining the necessary species through investigation of the Jacobian, and (3) eliminating insignificant species and redundant reactions.

A species in a system may be neglected if changes in its concentration have only a negligible effect on the concentrations of the important species. For a reaction system described by eq 1, the relative importance of species i on the N important species can be determined by taking the sum of the squares of the normalized Jacobian elements of the system (evaluated locally):

$$B_i = \sum_{n=1}^{N} \left(\frac{\partial \ln f_n}{\partial \ln c_i} \right)^2 \tag{57}$$

The species c_i can be neglected when it is found that $B_i < B$, where B is a small parameter reflecting the desired accuracy of the model. Note that this is an iterative procedure, as both important and necessary species must be insensitive to the species to be neglected; in effect, the summation in eq 57 is extended to include all species subsequently classified as necessary. Further simplification is possible by eliminating the redundant reactions, through principal component analysis of the rate sensitivity matrix,[55] $\mathbf{F}$, which has elements

$$F_{ij} = \frac{\partial \ln f_i}{6 \ln k_j} = \frac{\nu_{ij} R_j}{f_i} \tag{58}$$

where ν_{ij} is the stoichiometric coefficient of species i in reaction j, R_j is the rate of reaction j, k_j is the rate constant for reaction j, and f_i is the rate of production of species i. The reactions whose contributions, on the basis of the eigenvalues of $\mathbf{F}^{T}\mathbf{F}$, are below a desired precision threshold may be eliminated in that region.

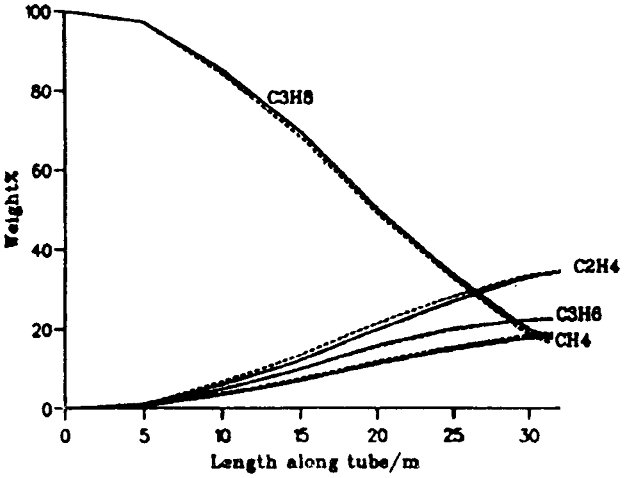


Figure 3. Weight percent of high-yield pyrolysis products as a function of reactor position for a full mechanism (solid line), 122-step mechanism (coincides with the solid line), and 50-step mechanism (dashed line). Both the 122- and 50-step mechanisms provide accurate results. Reprinted with permission from ref 52. Copyright 1995 American Chemical Society.

To ensure the accuracy of the reduced model, either the full model must be solved, or extensive data must be available to evaluate the sensitivity matrixes. In principle, only the important species need to be tracked in every region; however, to have continuity, any species necessary in one region must be tracked in every region. If more information is desired and more important species are designated, the number of necessary species also increases, and the extent of reduction achieved by sensitivity analysis decreases. Thus, in many cases, the sensitivity analysis approach is used in conjunction with the well-known quasi-steady-state approximation. In this manner, reduction by sensitivity analysis has been applied to combustion[53,54,56-59] and pyrolysis systems.[51,52,60] Sensitivity analysis also provides the basis for other reported reduction techniques such as regional analysis,[61] ridge regression analysis,[62] and genetic algorithms.[63]

A propane pyrolysis system, consisting of 422 reactions and 48 species,[1] was reduced using sensitivity analysis.[52] Eight important species are designated, leading to eleven necessary species. Examination of the reactions results in a 122-reaction mechanism and a 50-step mechanism. The 122-step mechanism is indistinguishable from the full system, while for the low-yield products the 50 step mechanism shows significant deviation (Figures 3 and 4).

Further order reduction is possible by applying the quasi-steady-state approximation to 12 of the species in the reduced system. The resulting differential–algebraic equation system produces results identical to those shown in Figures 3 and 4. In practice, even for the simpler 50-step mechanism, the resulting algebraic equations become so complicated that no computational benefit is gained by removing some of the differential equations.

V. Time-Scale Analysis

The dynamic behavior of reaction systems often contains multiple time scales; after an initial transient period, some fast reactions can be considered nearly instantaneous relative to the remaining slow ones. This is the basis of the quasi-steady-state approximation,[64] which has been successfully used for many reaction systems, such as enzyme catalysis[65] and combustion.[66]

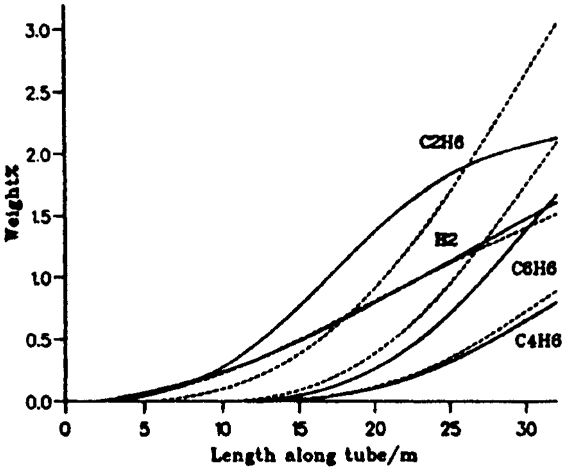


Figure 4. Weight percent of high-yield pyrolysis products as a function of reactor position for a full mechanism (solid line), 122-step mechanism (coincides with the solid line), and 50-step mechanism (dashed line). The 50-step mechanism shows significant deviation from the full model. Reprinted with permission from ref 52. Copyright 1995 American Chemical Society.

For a given quasi-steady-state (fast) species, c_s, the differential eq 1 changes from

$$\frac{\mathrm{d}c_s}{\mathrm{d}t} = f_s(c_1,c_2,...,c_n;\mathbf{k}) \tag{59}$$

into

$$f_s(c_1,c_2,...,c_n;\mathbf{k}) = 0 \tag{60}$$

It should be noted that eq 60 does not imply that $\mathrm{d}c_s/\mathrm{d}t = 0$, but rather that $\mathrm{d}c_s/\mathrm{d}t$ is dependent on the changes of the other concentrations with time,[67] as seen by the total time derivative of $f_s = 0$:

$$\frac{\mathrm{D}f_s}{\mathrm{D}t} = \frac{\partial f_s}{\partial c_1}\frac{\mathrm{d}c_1}{\mathrm{d}t} + \frac{\partial f_s}{\partial c_2}\frac{\mathrm{d}c_2}{\mathrm{d}t} + ... + \frac{\partial f_s}{\partial c_n}\frac{\mathrm{d}c_n}{\mathrm{d}t} = 0 \tag{61}$$

The concentrations of the fast species change with time, but these species can be described by algebraic relations instead of differential equations.

The generalized implementation of the technique is difficult because the identification of fast and slow reactions (difficult in itself) does not clearly indicate which are the true fast and slow species; thus, the reduced model may not be a valid approximation of the reaction kinetics.[68-72] There is a need for a systematic method that takes advantage of the different time scales, as the quasi-steady-state method is a proven reduction technique and the detail provided by such models gives insights into physical phenomena lost by other lumped models.[73,74]

A. Algebraic Approximation of the Inertial Manifold

When the quasi-steady-state approximation is analyzed from a geometrical view in phase space, it can

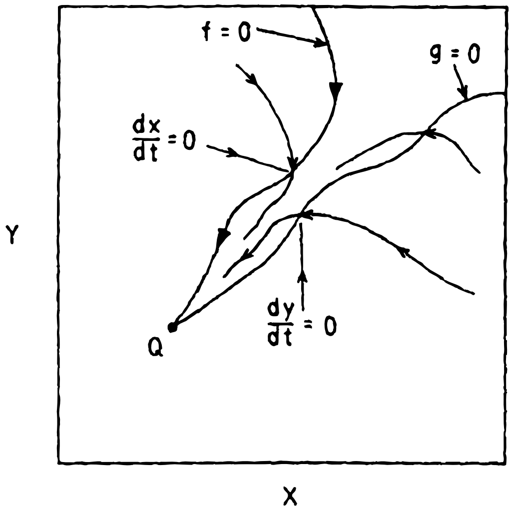


Figure 5. Schematic of the quasi-steady-state approximation for a system of two species. The *x* × *y* plane represents phase space. The system is d*x*/d*t* = *f* and d*y*/d*t* = *g*. Constrained motion (QSSA) with *f* = 0 is shown by heavy arrows. Equilibrium, *f* = *g* = 0, is point Q. Reprinted with permission from ref 67. Copyright 1988 American Institute of Physics.

be seen that, after an initial transient, the dynamics of the system are restricted to a lower dimensional manifold, thereby reducing the order.[67,75] Figure 5 shows the evolution of a two-species system to the equilibrium point Q. For this system, it is seen that the $f = 0$ curve is a good approximation to the true dynamic behavior of the system. For higher dimensional systems, the relaxation of a system of chemical reactions can be viewed as a nested hierarchy of inertial manifolds.[76,77] It is possible to model the dynamics through a sequence of inertial manifolds, each of decreasing dimension. As with the quasi-steady-state approximation, the user of the model is often interested only in the slowest dynamics of a system, given by the lowest dimensional manifold.

The inertial manifold can be approximated iteratively starting from equilibrium or steady-state approximations.[67,75,76,78,79] To estimate the slow manifold, it is necessary to describe the evolution of the system in phase space. Trajectory equations for intermediate species, which eliminate the time dependence, express those species in terms of a progression species, c_p, which is not an intermediate or a catalyst in the system.

$$c_i' = \frac{\mathrm{d}c_i/\mathrm{d}t}{\mathrm{d}c_\mathrm{p}/\mathrm{d}t} = \frac{\mathrm{d}c_i}{\mathrm{d}c_p} = \frac{f_i(\mathbf{c};\mathbf{k})}{f_\mathrm{p}(\mathbf{c};\mathbf{k})} \qquad i = 1, ..., n \qquad i \neq p \tag{62}$$

Expressions for the intermediate species may then be found in terms of the trajectory equations

$$c_i = g_i(c_i', c_1, ..., c_{i-1}, c_{i+1}, ..., c_n; \mathbf{k}) \qquad i = 1, ..., n \qquad i \neq p \tag{63}$$

From eq 63, the manifold can be estimated through an iterative procedure, where the derivative and other species are evaluated from an initial guess to the solution

$$(c_i)_{j+1} = [g_i(c_i', c_1, ..., c_{i-1}, c_{i+1}, ..., c_n; \mathbf{k})]_j \tag{64}$$

The subscripts j and $j + 1$ indicate the iteration. In higher dimensional systems (>2), convergence toward the slow manifold is improved by linearizing the expressions about a fixed point $\hat{\mathbf{c}}^*$. The resulting expressions for the species are

$$(c_i)_j = c_i^* + (\epsilon_i)_j \tag{65}$$

which result in a matrix equation for the error in iteration $j + 1$ as a function of the error in iteration j

$$\epsilon_{j+1} = \mathbf{M}\epsilon_j \tag{66}$$

The matrix **M** is square with diagonal elements

$$M_{ii} = \frac{\partial g_i}{\partial (c_i^*)'} \frac{\mathrm{d}}{\mathrm{d}c_\mathrm{p}} \tag{67}$$

and off-diagonal elements

$$M_{ij} = \frac{\partial g_i}{\partial c_j^*} \tag{68}$$

Iterations are then performed on the error terms. Appropriate initial guesses are based on equilibrium and steady-state approximations. In higher (>2) dimensional systems, these approximations are the intersections of the nullclines, which are the surfaces described by

$$f_j(\mathbf{c};\mathbf{k}) = 0 \qquad j = 1, ..., n \tag{69}$$

Initial guesses are then based on the nullcline eq 69 being solved for a species other than the progression species:

$$c_i = N_j(c_1, ..., c_{i-1}, c_{i+1}, ..., c_n; \mathbf{k}) \qquad i \neq p \tag{70}$$

It is possible to also extract a transient surface of dimension $n - 1$ using similar techniques. This requires that the fastest species, c_1, be written in terms of the other independent species as

$$c_1 = C(c_2, ..., c_n) \tag{71}$$

and differentiated with respect to time

$$\frac{\mathrm{d}c_1}{\mathrm{d}t} = \sum_{k=2}^{n} \frac{\partial C}{\partial c_k} \frac{\mathrm{d}c_k}{\mathrm{d}t} \tag{72}$$

This equation is rearranged in a manner similar to that of eq 63 to obtain an equation that can be used to iteratively solve for the surface.

$$[C(c_2, ..., c_n)]_{j+1} = g\left(c_2, ..., c_n, \frac{\partial C_j}{\partial c_2}, ..., \frac{\partial C_j}{\partial c_n}\right) \tag{73}$$

An appropriate initial guess is the nullcline surface created by the change of the next fastest variable being set to 0 (eq 70). This surface describing the transient flow can be found when the Jacobian has real eigenvalues; complex eigenvalues indicate oscillatory relaxation, and the direction of this flow is undefined.

This method was used to analyze the Lindemann mechanism[67] and enzyme kinetics.[75,76,78-80] Equations for systems of 3 dimensions reduced to 2 and 1 dimension(s) were developed, and novel dynamic phenomena were revealed.[79] The approach may be used to predict the evolution of the system or assign experimental results to the appropriate time scale, enabling determination of the rate constants.[76,79]

A more localized approach has shown applicability toward more general reaction systems.[81] By evaluating the Jacobian of **f** (eq 1), points may be found where components in the directions of the eigenvectors corresponding to the n_f fastest time scales vanish. Then, reduction to a system of dimension $\hat{n} = n - n_f$ is possible.

Let **V** be the matrix of eigenvectors of the Jacobian, ordered by decreasing values of the real parts of the corresponding eigenvalues

$$\mathbf{V} = (\mathbf{v}_1\ \mathbf{v}_2\ ...\ \mathbf{v}_n) \tag{74}$$

and let its inverse, $\mathbf{V}^{-1}$, be represented as

$$\mathbf{V}^{-1} = \begin{pmatrix} \tilde{\mathbf{v}}_1 \\ \tilde{\mathbf{v}}_2 \\ \vdots \\ \tilde{\mathbf{v}}_n \end{pmatrix} \tag{75}$$

Then, the slow manifold is defined by

$$\mathbf{Wf} = 0 \tag{76}$$

where **W** is formed by the last n_f rows of $\mathbf{V}^{-1}$. For cases of poorly conditioned matrixes, it may be better to work in terms of the Schur vectors, defined by **Q**

$$\mathbf{Q}^T \mathbf{f}_c \mathbf{Q} = \mathbf{N} \tag{77}$$

where **N** is the diagonal vector of the eigenvalues, ordered by descending real parts. In this case, $\mathbf{Q}^T$ would have the same role as $\mathbf{V}^{-1}$, and the last n_f rows would define the slow manifold. To obtain numerical values of points of the manifold, the n_f equations of eq 76 must be solved, along with $n - n_f$ additional equations. The system that must be solved takes the form

$$G(c,s) = \begin{pmatrix} \mathbf{W(c)\ f(c)} \\ \mathbf{P(c,s)} \end{pmatrix} = 0 \tag{78}$$

where **P**(**c**,**s**) are the additional $n - n_f$ parameter equations and **s** are additional variables. The equations **P** and variables **s** specifically consist of the following: n_e (the number of conserved quantities in the system) conservation relations, **g**, and corresponding parameters, $\mathbf{s}_e$; and $\hat{n}$ concentration equations, **h**, for species chosen to describe the progress of the reaction, and the corresponding parameters, $\mathbf{s}_p$. Thus, the system of parameter equations takes the form

$$\mathbf{P(c,s)} = \begin{pmatrix} \mathbf{g(c,s_e)} \\ \mathbf{h(c,s_p)} \end{pmatrix} = 0 \tag{79}$$

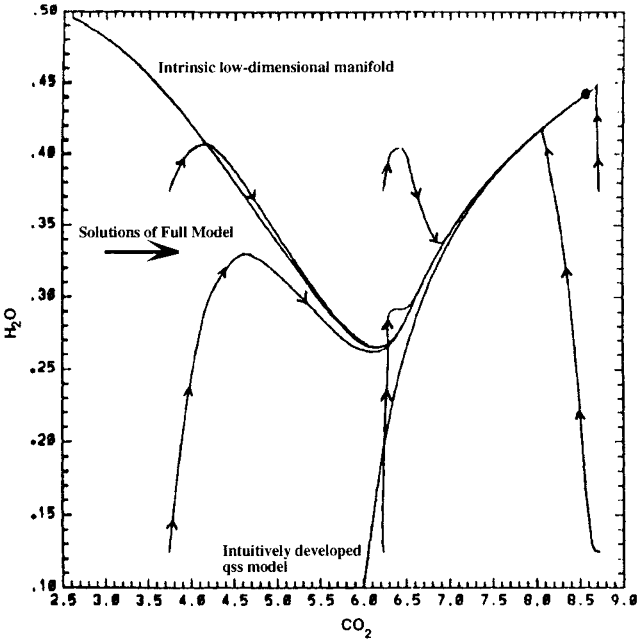


Figure 6. H_2O concentration plotted as a function of CO_2 concentration in the CO/H_2/air combustion system. The low-dimensional manifold better approximates the full simulations (shown by arrows) than a QSSA model. Reprinted with permission from ref 81. Copyright 1992 Elsevier Science Inc.

The solution may be found by starting from fixed values for the parameters, **s**, and solving eq 78 by Newton's method.

This method gives purely numerical results for the slow manifold. Such an approach is useful in solving complicated fluid dynamics equations by Monte Carlo methods.[82,83] The solution to one full simulation is required, but the reduced models then give solutions applicable to a wide range of initial conditions. Also, it should be noted that this approach has a larger range of applicability than intuitively developed QSSA models.

When this method was applied to a CO/H_2/air combustion system of 13 species and 67 reactions,[2] both 1- and 2-dimensional manifolds were obtained.[81] The 1-dimensional manifold compared to an intuitively developed quasi-steady-state model is shown in Figure 6. On the basis of the trajectories of the full solution from different initial conditions, the reduced manifold is shown to estimate the dynamic behavior over a wider range of composition space than a QSSA model.

A more general approach to the approximation of the inertial manifold is the method of algebraic sets.[77] This method applies for reaction systems which are partitioned into

$$\frac{d\mathbf{y}}{dt} = \mathbf{f(y,z;k)} \tag{80}$$

$$\epsilon \frac{d\mathbf{z}}{dt} = -\mathbf{Az} - \mathbf{g(y,z;k)} \tag{81}$$

where **y** and **z** are the vectors of slow (dimension n_s) and fast (dimension n_f) species, respectively, ϵ is a diagonal matrix containing small positive numbers ϵ_i, and **A** is a positive diagonal matrix. A restriction on the applicability is that there must be a dissipation term which is linear in $\mathbf{z}$, although nonlinear terms in $\mathbf{z}$ may also be present. The goal of the method is to obtain an algebraic expression for $\mathbf{z}$ that approximates the real dynamic behavior of the fast variables.

The formal solution of the equation for the fast variables (eq 81) is

$$\mathbf{z}(0) = \mathbf{e}^{\mathbf{A}t/\epsilon}\, \mathbf{z}(t) - \frac{1}{\epsilon}\int_t^0 \mathrm{e}^{\mathbf{A}\tau/\epsilon}\, \mathbf{g}[\mathbf{y}(\tau),\mathbf{z}(\tau)]\, \mathrm{d}\tau \quad (82)$$

where the notation $1/\epsilon$ is used to represent the inverse of the diagonal matrix. By taking $t \rightarrow -\infty$ and assuming $\mathbf{z}(t)$ is bounded, eq 82 simplifies to

$$\mathbf{z}(0) = -\frac{1}{\epsilon}\int_{-\infty}^0 \mathrm{e}^{\mathbf{A}\tau/\epsilon}\, \mathbf{g}[\mathbf{y}(\tau),\mathbf{z}(\tau)]\, \mathrm{d}\tau \qquad (83)$$

To obtain the solution, the vectors $\mathbf{y}$, $\mathbf{z}$, and $\mathbf{g}$ must be expressible as a convergent power series in time. This is possible if the solution is analytic in time. On the real time axis, this is indeed the case, since chemical systems are inherently bounded; in the complex t-plane, it can be shown that the solution is analytic within a finite strip of width λ.[84] Thus, series expressions of $\mathbf{y}$, $\mathbf{z}$, and $\mathbf{g}$ are possible for $t \in [-\lambda,0]$.

For each fast variable, the integral (eq 83) is broken down to separate the initial transient behavior from the inertial manifold:

$$z_i(0) = -\frac{1}{\epsilon_i}\int_{-\infty}^{-\lambda} \mathrm{e}^{A_i\tau/\epsilon_i}\, g_i[\mathbf{y}(\tau),\mathbf{z}(\tau)]\, \mathrm{d}\tau - \frac{1}{\epsilon_i}\int_{-\lambda}^{0} \mathrm{e}^{A_i\tau/\epsilon_i}\, g_i[\mathbf{y}(\tau),\mathbf{z}(\tau)]\, \mathrm{d}\tau \quad (84)$$

The first integral corresponds to the transient behavior, and it is always bounded by an exponentially small term, leaving

$$z_i(0) = -\frac{1}{\epsilon_i}\int_{-\lambda}^{0} \mathrm{e}^{A_i\tau/\epsilon_i}\, g_i[\mathbf{y}(\tau),\, \mathbf{z}(\tau)]\, \mathrm{d}\tau \qquad (85)$$

Equation 85 can be solved for each fast variable, using a series expansion for $\mathbf{g}$

$$g_i(t) = \sum_{n=0}^{\infty} g_i^{(n)}(\mathbf{y}(0),\mathbf{z}(0))\frac{t^n}{n!} \qquad (86)$$

so that an algebraic approximation for a fast variable z_i can be found

$$z_i(0) = c_0^i\, g_i^{(0)}(\mathbf{y}(0),\mathbf{z}(0)) + c_1^i\, g_i^{(1)}(\mathbf{y}(0),\mathbf{z}(0)) + \ldots \qquad (87)$$

where

$$c_n^i = -\frac{1}{\epsilon_i}\int_{-\lambda}^{0} \mathrm{e}^{A_i\tau/\epsilon_i}\, \frac{\tau^n}{n!}\, \mathrm{d}\tau \qquad (88)$$

The points $\mathbf{z}(0)$ and $\mathbf{y}(0)$ may be replaced by a general point on the manifold, $\mathbf{z}$ and $\mathbf{y}$, since the inertial manifold is an invariant set under the dynamics. The only requirement for λ is that $\lambda > 0$; then, after integration of eq 88 the associated exponential terms vanish as $\epsilon \rightarrow 0$:

$$\lim_{\epsilon\rightarrow 0} \mathrm{e}^{-\lambda a/\epsilon} = 0 \qquad (89)$$

Thus, algebraic expressions can be found approximating each fast variable z_i so that

$$z_i = F_i(\mathbf{y}) \qquad (90)$$

and the dimension of the system is reduced from $(n_\mathrm{f} + n_\mathrm{s})$ to n_s.

Estimations of invariant manifolds have primarily been used to analyze and generate reduced models of enzyme kinetics.[75−80] Novel dynamic phenomena have been revealed,[79] and the reduced kinetics have been incorporated into models of reaction−diffusion systems.[77] Enzyme kinetics have the advantage that the equation for the fast intermediate species can be written in the form of eq 81; furthermore, it is known from the outset which are the true fast and slow species. The use of algebraic sets is not currently possible for systems where the true fast and slow species have not been identified. For more general reaction systems, a localized approach is possible to evaluate the manifold numerically; this method has been used to generate numerical descriptions for a combustion system.[81]

B. Computational Singular Perturbation

Computational singular perturbation[59,85−87] produces simplified nonstiff models through the analysis of the time scales. The method partitions the system so that, at a given time, only certain dynamic modes are active. *Active* modes are those which are slow and yield dynamic information about the system. The other modes are either exhausted or dormant. *Exhausted* modes are those which have decayed due to competing fast consumption and generation reactions so that their contribution is negligible during the time period of interest. *Dormant* modes are those which are much slower than the active modes, so that for the time period of interest they have negligible effect on the active modes. Computational singular perturbation solves a system of equations along a specific trajectory by generating reduced models applicable for given regions. The quantities obtained from computational singular perturbation may be used to investigate further order reduction possibilities.[88,89]

The kinetics of a reaction system (eq 1) can be expressed as

$$\mathbf{f}(\mathbf{c},\mathbf{k}) = \sum_{r=1}^{R} \mathbf{s}_r F^r(\mathbf{c},\mathbf{k}) \qquad (91)$$

where R is the number of reactions, $\mathbf{s}_r$ is the stoichiometric vector, and F^r is the reaction rate of the rth reaction. This physical representation is not suitable for analyzing dynamic modes, as each term r does not correspond to a different time scale. However, the n-dimensional vector $\mathbf{f}$ can be equivalently expressed in terms of n linearly independent column basis vectors $\mathbf{a}_j$ ($j = 1, 2, ..., n$) corresponding to distinct dynamic modes:

$$\mathbf{f}(\mathbf{c},\mathbf{k}) = \sum_{j=1}^{n} \mathbf{a}_j f^j(\mathbf{c},\mathbf{k}) \qquad (92)$$

The amplitude of the ith mode, f^i, is given by where

$$f^i(\mathbf{k},\mathbf{c}) = \mathbf{b}^i\mathbf{f} = \sum_{r=1}^{R} B^i_r F^r(\mathbf{c},\mathbf{k}) \qquad i = 1, 2, ..., n \qquad (93)$$

$$B^i_r = \mathbf{b}^i\mathbf{s}_r \qquad i = 1, 2, ..., n \qquad r = 1, 2, ..., R \qquad (94)$$

The row vectors $\mathbf{b}^i$ form a matrix which is the inverse of the matrix formed by the $\mathbf{a}_j$ column vectors. This can be expressed as

$$\mathbf{b}^i\mathbf{a}_j = \delta^i_j \qquad i, j = 1, 2, ..., n \qquad (95)$$

where σ^i_j is the Kronecker delta ($\delta^i_j = 1$ if $i = j$, and $\delta^i_j = 0$ otherwise). Thus, once the $\mathbf{a}_j$ vectors are chosen, $\mathbf{b}^i$ can be computed. For each region, the basis vectors $\mathbf{a}_j$ are computed from an initial guess, which may originate from the physical representation or a previously determined mode. Iterations around a two-step refinement process are then required to generate satisfactory basis vectors.[90]

When the $\mathbf{a}_j$ vectors have the desired effect, the modes represent different time scales and can be ranked accordingly. Thus, at a given time point, only one mode, j, is active and the system of differential equations (eq 92) becomes

$$\frac{d\mathbf{c}}{dt} = \mathbf{a}_j f^j(\mathbf{k},\mathbf{c}) \qquad (96)$$

where the $i < j$ modes are exhausted, and the $i > j$ modes are dormant. Equation 96 involves fewer reaction terms, and it is not stiff. Model order reduction occurs if one or more of the concentrations are unaffected by the active mode. For these species, the concentrations can be derived from the exhausted modes, on the basis of the equations

$$f^i(\mathbf{k},\mathbf{c}) = 0 \qquad i = 1, 2, ..., j - 1 \qquad (97)$$

Further simplification and order reduction are possible on the basis of the analysis of the terms in the active and exhausted modes, in a manner similar that of to sensitivity analysis. This is referred to as finding the *minimum set*,[88] which may be used for further investigations along the same trajectory. The insignificant reactions may be neglected for a region, and if some species are found not to participate in any region, these may be removed from the model completely. An advantage of computational singular perturbation is that data from a simplified system may be used to determine the importance of reactions, in contrast to sensitivity analysis which requires data from the full system. Computational singular perturbation works best in the asymptotic limit of sharply divided regions, where $f_j \gg f_i$ ($i = 1, ... n$; $i \neq j$). For these cases, the coupling between modes is negligible. For the boundary layers, a correction may be applied to improve the accuracy of the model.[88]

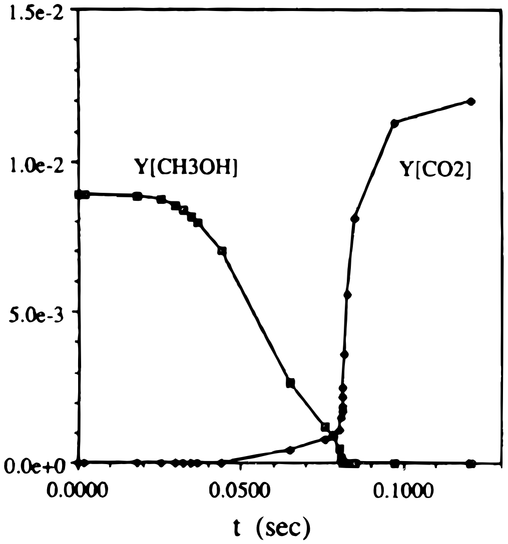


Figure 7. CSP results of the mass fractions of methanol and CO_2 as a function of time. Reprinted with permission from ref 86. Copyright 1992 The Combustion Institute.

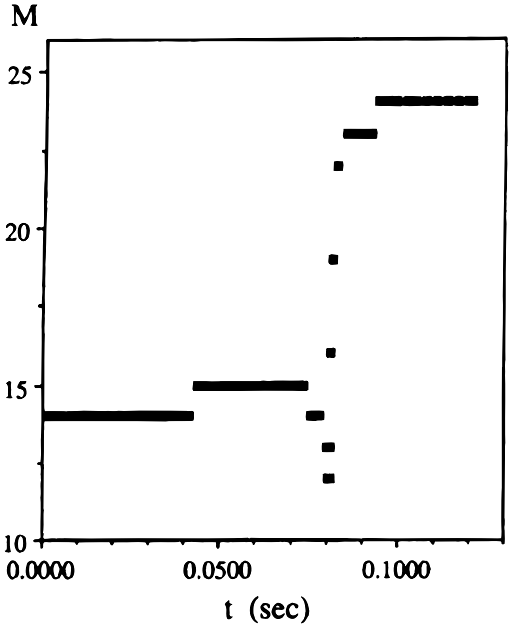


Figure 8. Number of reduced modes as a function of time. The reduced modes correspond to the extent of order reduction. Reprinted with permission from ref 86. Copyright 1992 The Combustion Institute.

Computational singular perturbation (CSP) was applied to a methanol combustion system[86] consisting of 30 species and 173 reactions.[91] The CSP results of the important species are shown in Figure 7. The extent of order reduction is indicated by the number of exhausted modes (Figure 8). The interval between markers in Figures 7−9 represents 24 time steps used by the CSP algorithm to ensure accuracy within each region. The minimum set of this system, for the time interval of interest, contains 16 of the 30 original species. This reduced system produces results nearly identical to those of the full model (Figure 9).

Computational singular perturbation has been primarily used in the reduction of flame kinet-

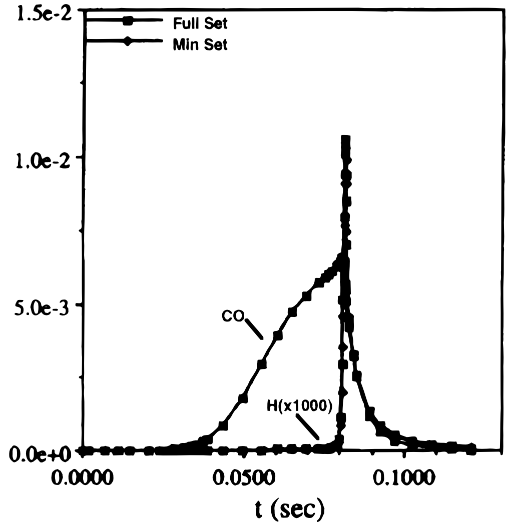


Figure 9. Mass fractions of CO and H as a function of time for the model consisting of the minimum set of species and for the full model. The lines essentially coincide, indicating agreement of the two models. Reprinted with permission from ref 86. Copyright 1992 The Combustion Institute.

ics.[59,86,87] The method takes advantage of modern computational power to find the basis vectors iteratively and makes the necessary corrections to solve for the solution of a complex model along a specific trajectory. It does not require prior expert knowledge of the system of interest. Care must be taken in choosing intervals over which to apply the method because the size of the regions cannot be determined a priori.

C. Linear Transformation into Standard Two-Time-Scale Form

Another approach to exploiting time scales is the development of algorithms for systematic conversion of the model into one that satisfies the assumptions of the quasi-steady-state approximation. The key to systematic order reduction lies in the transformation of a model to the standard two-time-scale form of singular perturbation theory.[92] The quasi-steady-state approximation for reaction systems was first recognized as a singular perturbation problem by Bowen.[93] In the standard two-time-scale form, eq 1 is separated into fast and slow species. The model of the reaction system is expressed as

$$\frac{\mathrm{d}\mathbf{y}}{\mathrm{d}t} = \mathbf{f}(\mathbf{y},\mathbf{z},\epsilon,\mathbf{k}), \quad \mathbf{y}(t_0) = \mathbf{y}^0 \tag{98}$$

$$\epsilon\frac{\mathrm{d}\mathbf{z}}{\mathrm{d}t} = \mathbf{g}(\mathbf{y},\mathbf{z},\epsilon,\mathbf{k}), \quad \mathbf{z}(t_0) = \mathbf{z}^0 \tag{99}$$

where $\mathbf{y}$ is the concentration vector of slow species, $\mathbf{z}$ is the concentration vector of fast species, and ϵ is the small perturbation parameter representing the rate ratio of the slow to fast species. Model reduction is possible when ϵ approaches zero. Equation 99 then becomes an algebraic expression

$$0 = \mathbf{g}(\hat{\mathbf{y}}(t),\hat{\mathbf{z}}(t),0,\mathbf{k}) \tag{100}$$

where the circumflex above variables represents those in the reduced system. There exists $t_1 \geq t_0$ such that the approximation (eq 100) is valid over an interval $[t_1, T]$ if the following conditions are true:[92] (1) In the limit $\epsilon \rightarrow 0$, the associated algebraic eq 100 must have isolated explicit roots with respect to $\hat{\mathbf{z}}$. (2) Defining $\mathbf{z}^* = \mathbf{z} - \hat{\mathbf{z}}$ as the boundary layer correction, the equilibrium of this boundary layer system expressed in the fast time scale ($\tau = t/\epsilon$)

$$\frac{\mathrm{d}\mathbf{z}^*}{\mathrm{d}\tau} = \mathbf{g}(\mathbf{y}^0,\mathbf{z}^*+\hat{\mathbf{z}}(t_0),0,\mathbf{k}) \tag{101}$$

must have an equilibrium state ($\mathbf{z}^* = 0$) which is asymptotically stable uniformly in $\mathbf{y}^0$ and t_0, and $\mathbf{z}^0 - \hat{\mathbf{z}}(t_0)$ must belong to its domain of attraction. (3) The eigenvalues of $\partial\mathbf{g}/\partial\mathbf{z}$ evaluated at the phase point $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ for $\epsilon = 0$ have strictly negative real parts.

These conditions are closely related to the estimation of the slow manifold of a system. The first ensures that an estimation for the associated nullclines exist (eq 70), and conditions 2 and 3 force the stability of the fast system. The trajectories of the fast subsystem must contract onto the slow manifold in a uniform manner.

In their initial definition, the models of reaction systems are not easily partitioned to obtain equations of the form of eqs 98 and 99 satisfying the above conditions. Certain types of reaction systems can be expressed in the standard form through a linear transformation. A method specific for biochemical pathways was presented by Schauer and Heinrich;[94] and for more generalized types of reaction systems, van Breusegem and Bastin presented a method that is described below.[95]

A linear stoichiometric matrix is extracted from eq 1 by writing it in the form

$$\frac{\mathrm{d}\mathbf{c}}{\mathrm{d}t} = \mathbf{CK}\Phi(\mathbf{c}) \tag{102}$$

where $\mathbf{C}$ is the linear stoichiometric matrix, $\mathbf{K}$ is a diagonal matrix of rate constants, and Φ is the matrix of rate expressions (based on mass action kinetics, for example). Once fast and slow reactions are identified, $\mathbf{C}$ is partitioned into submatrixes representing fast species in fast reactions ($\mathbf{C}_{\mathrm{ff}}$), fast species in slow reactions ($\mathbf{C}_{\mathrm{fs}}$), and slow species in slow reactions ($\mathbf{C}_{\mathrm{ss}}$); by definition, slow species are independent of the fast reactions. The set of differential equations for the reaction system then becomes

$$\frac{\mathrm{d}\mathbf{c}_{\mathrm{f}}}{\mathrm{d}t} = \mathbf{C}_{\mathrm{ff}}\mathbf{K}_{\mathrm{f}}\Phi_{\mathrm{f}}(\mathbf{c}_{\mathrm{f}}) + \mathbf{C}_{\mathrm{sf}}\mathbf{K}_{\mathrm{s}}\Phi_{\mathrm{s}}(\mathbf{c}) \tag{103}$$

$$\frac{\mathrm{d}\mathbf{c}_{\mathrm{s}}}{\mathrm{d}t} = \mathbf{C}_{\mathrm{ss}}\mathbf{K}_{\mathrm{s}}\Phi_{\mathrm{s}}(\mathbf{c}) \tag{104}$$

where $\mathbf{c}_{\mathrm{f}}$ and $\mathbf{c}_{\mathrm{s}}$ represent concentration vectors of the *potentially* fast and slow species. The perturbation parameter is defined as the ratio of the average slow rate constant $\bar{k}_{\mathrm{s}}$ to the average fast rate constant $\bar{k}_{\mathrm{f}}$:

$$\epsilon = \bar{k}_{\mathrm{s}}/\bar{k}_{\mathrm{f}} \tag{105}$$

This yields an apparent two-time-scale system

$$\epsilon \frac{d\mathbf{c}_f}{dt} = \mathbf{C}_{ff}\alpha_f\Phi_f(\mathbf{c}_f) + \epsilon\mathbf{C}_{sf}\mathbf{K}_s\Phi_s(\mathbf{c}) \qquad (106)$$

$$\frac{d\mathbf{c}_s}{dt} = \mathbf{C}_{ss}\mathbf{K}_s\Phi_s(\mathbf{c}) \qquad (107)$$

where α is a diagonal matrix of the scaled fast reaction rate constants

$$\alpha_{ii} = \epsilon k_{f,i} \qquad (108)$$

In most cases, condition 1 is not satisfied for eq 106 as $\epsilon \rightarrow 0$, meaning that not all the potential fast species are truly fast. In some cases, the true fast variables may be found through a linear transformation of the reactants

$$\xi = \mathbf{Tc} \qquad (109)$$

where **T** is defined so that

$$\mathbf{TC}_{ff} = \begin{pmatrix} \mathbf{A}_{11} & \mathbf{A}_{12} \\ 0 & \mathbf{A}_{13} \\ 0 & 0 \end{pmatrix} \qquad (110)$$

The key is to create a matrix for the fast reactions such that its first ρ nonzero rows are linearly independent (and thus form a matrix of rank ρ); this increases the likelihood that a system will satisfy condition 1. The transformed system becomes

$$\epsilon \frac{d\xi_f}{dt} = \tilde{\mathbf{A}}\mathbf{a}_f\Phi_f(\xi) + \epsilon\tilde{\mathbf{B}}\mathbf{K}_s\Phi_s(\xi) \qquad (111)$$

$$\frac{d\xi_s}{dt} = \bar{\mathbf{B}}\mathbf{K}_s\Phi_s(\xi) \qquad (112)$$

where **A** and **B** are the stoichiometric matrixes in the transformed system. The order of the system can be reduced by setting ϵ equal to 0. If condition 1 is satisfied, then there are several possible reduced models, and valid models must satisfy conditions 2 and 3.

The transformation technique works best for linear systems and weakly coupled nonlinear systems. Since only the stoichiometric matrixes are considered, coupled nonlinear reactions will cause degeneracies and erroneously identify fast species in solving for the steady-state solution. In these cases, condition 1 is not satisfied, even after the described transformation of variables. However, the conditions of the standard two-time-scale form ensure the applicability of the reduced models after long times, and invalid models are easily identified without the use of the full model. The reduced models are nonstiff, thereby reducing computation time and enabling solution by more accessible computers. The reduced models are at least as accurate as intuitively developed quasi-steady-state models and may even provide better approximations in some cases.[96] Figure 10 shows the comparison of reduced models for the simple enzyme-catalyzed reaction

$$X_1 + X_2 \rightleftharpoons X_3 \rightarrow X_4 + X_2$$

If the thickness of the boundary layer or the extent of model reduction is not satisfactory, improved models may be generated from a refined perturbation method which incorporates the Shanks transformation of a power series.[97] Once a system of reactions has been transformed to the standard two-time-scale form, the fast variables, **z**, may be expressed as a power series:

$$z_i = z_i^{(0)} + \epsilon z_i^{(1)} + \epsilon^2 z_i^{(2)} + \ldots \qquad i = 1, \ldots, n_f \qquad (113)$$

The direct reduction method described above, similar to the quasi-steady-state approximation, only retains the $z_i^{(0)}$ term, yet improved models may be generated by retaining the $z_i^{(1)}$ term. Retaining higher (≥ 2) order terms is not desirable as the accuracy does not improve significantly enough to justify the higher computational cost. The Shanks transformation[98]

$$T\{S_n\} = \frac{S_n S_{n-2} - S_{n-1}^2}{S_n + S_{n-2} - 2S_{n-1}} \qquad (114)$$

where S_n is the nth partial sum of a series, is then used to accelerate the convergence of the resulting series for z_i (eq 113), as it may be only asymptotically convergent or even divergent. When applied to a hydrogen combustion system, this refinement reduced the thickness of the boundary layer, and increased the extent of model order reduction over ordinary quasi-steady-state models.[97]

VI. Summary

Model order reduction is important in analyzing complex chemical reaction networks. The differential equations are easier to solve if the number of independent species is reduced and, in some cases, if the time scales are decoupled. Reduction methods give valuable insights into the key reactions, species, and relationships in a complex system.

The choice of model order reduction method depends on the accuracy required for the modeling task, the structure of the reaction system, and the extent of available kinetic information. For linear reaction systems, all of the described methods—lumping, sensitivity analysis, and time-scale analysis—perform adequately if enough kinetic information is available about the system. However, these methods have not yet been fully developed for nonlinear systems.

Continuum lumping applies only to a narrow class of systems where the reacting mixture can be approximated as a continuous distribution and the species decay by the same reaction order. All the reactants are combined into a single lump, and the disappearance of that lump is tracked. Tracking only this single lump simplifies the dynamic model, and the lumped kinetics enable its use in simple reactor and transport models. The strength of the treatment is that only a small set of experimental data is required to fit the parameters of the reduced model, as specific reactions and component concentrations do not need to be known. However, this is a limitation for applications that require information about specific concentrations or reaction types, as such

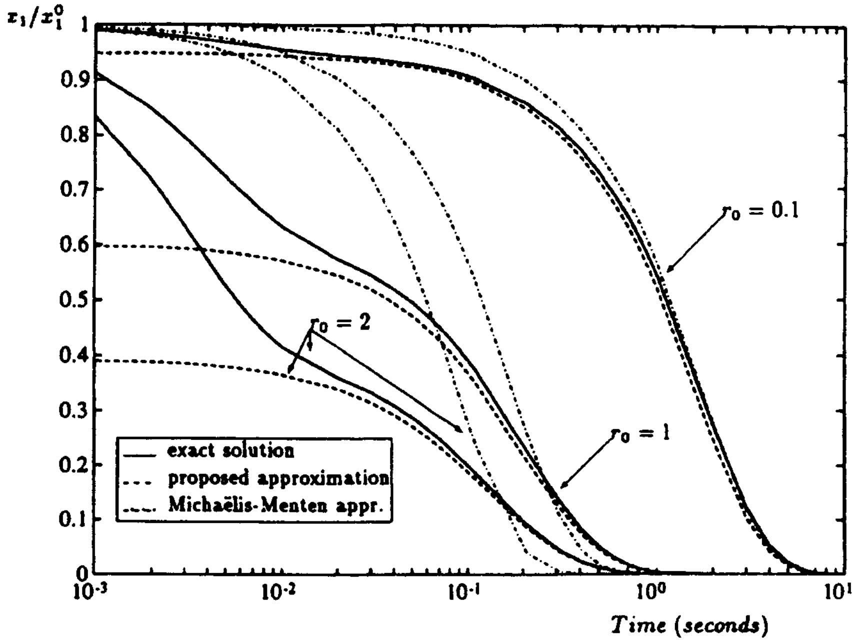


Figure 10. For various enzyme-to-substrate ratios (x_2/x_1), the singular perturbation model is shown to better simulate the full enzymatic reaction system than an intuitively developed reduced model (Michaelis–Menten approximation). Reprinted with permission from ref 96. Copyright 1993 University of Louvain.

information is not easily extracted from or incorporated into continuum lumps.

When a kinetic scheme is known, discrete lumping is possible. Lumped models can be determined from the equations describing the reaction kinetics for systems of moderate nonlinearity. The number of independent species is reduced, and the error introduced can be estimated. However, the generated reaction schemes may still contain multiple time scales, and information about a specific component (which may be necessary for process monitoring or control) can be extracted only for certain reaction structures.

Model order reduction through sensitivity analysis is feasible when the complete reaction scheme and its full solution (or extensive data) are known. In sensitivity analysis, one may specify which species need to be retained in the reduced model, as well as the desired accuracy. For given regions of the concentration space, the key species and reactions are identified, although the size of these regions cannot be determined a priori. Small time steps and comparisons to the full model are necessary to ensure the accurate modeling of the important species. The extent of order reduction decreases when more information must be retained.

Computational singular perturbation (CSP) builds on sensitivity analysis. By identifying the important modes that embody the different time scales of the reaction system, the method is able to perform model simplification in a manner similar to that of sensitivity analysis without the need for solutions to the full kinetic model. The stiffness in a region is reduced, and species at steady state are identified. CSP simplifies the system of differential equations by eliminating terms and ignoring species found to be insignificant for all regions of interest. As with sensitivity analysis, the size of these regions cannot be determined a priori, and the accuracy of the solutions in the boundaries cannot be ensured.

The standard two-time-scale form retains expressions, algebraic or differential equations, for all species in a reaction mechanism. A reduced model is developed that is guaranteed to be valid (in the limit of a particular system parameter $\epsilon \rightarrow 0$) after a pseudo-steady-state has been reached. This model will be nonstiff and of lower order. However, the transformation of a reaction system to the standard form can be applied systematically only to systems of low nonlinearity.

The method of invariant manifolds is also based on separating the time scales of a reaction system. When the relative scales are known, it is possible to determine the lowest dimensional manifold algebraically, and obtain the reduced equations for the slow behavior of a reaction system. In phase space, the method is also a valuable analysis tool, although for many complex systems the true fast and slow species are not known a priori.

As performance requirements and sensing technologies push the limits of both available data and required model precision for complex systems, model order reduction and simplification will play an important role in the study of complex reaction networks. The directions of further advances in model order reduction lie in developing improved techniques for general nonlinear systems, incorporating detailed kinetic mechanisms in lumping algorithms, combining several reduction methods, and transforming the equations representing reaction systems to standard forms for the identification of key species and the generation of reduced models.

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