Nonlinear Model Reduction of Chemical Reaction Systems

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A nonlinear model reduction method for nonisothermal reaction systems that exhibit dynamics in two different time scales owing to the presence of fast and slow reactions was developed. The method systematically identifies the independent algebraic constraints that define the low-dimensional state space where the slow dynamics of the reaction system are constrained to evolve. It also derives state-space realizations of the resulting differential algebraic system that describes the slow dynamics. This method is illustrated through the classic Michaelis-Menten reaction system, and is applied to an ozone decomposition reaction system and a reaction mechanism for esterification of carboxylic acid.

Introduction

Complex chemical reaction systems arise in a variety of processes, such as combustion, chemical-vapor deposition, fluid catalytic cracking, and biotechnological processes. The incorporation of detailed chemistry in the modeling of such processes is critical for design, optimization, and control. However, the use of such detailed models is hindered by several factors; first, a large number of kinetic parameters needs to be determined; second, such detailed models are inherently stiff due to the presence of several large and small kinetic parameters; finally, due to their high dimensionality the numerical simulation of such models is computationally demanding, especially when the kinetics are coupled with transport. Thus, it is desirable to develop a methodology to obtain reduced-order models of chemical reaction systems, which capture the time evolution of species composition and temperature with sufficient accuracy, and can be used for prediction and control.

There exists a vast literature on model reduction of reaction systems (see Okino and Mavrovouniotis (1998) for a very comprehensive recent review). The available modelreduction methods can be broadly classified as (1) lumping, (2) sensitivity analysis, and (3) time-scale analysis. In lumping, the original composition vector is lumped into a low-dimensional one such that the kinetic model is simplified (Bailey, 1972). Either a continuum (Aris and Gavalas, 1966; Astarita and Ocone, 1992) or a discrete [linear (Li and Rabitz, 1989; Wei and Kuo, 1969) or nonlinear (Li et al., 1994; Tomlin et al., 1994)] approach can be followed for this purpose, depending on the available data and the structure of the system. However, the difficulty in selecting/finding an appropriate lumping approach increases manifold for large nonlinear reaction systems, whereas there is also an inherent loss of information about individual species and reactions. Sensitivity analysis seeks to determine and retain only significant reactions and species (Petzold and Zhu, 1999; Rabitz et al., 1983; Siegneur et al., 1982; Turányi et al., 1989). Additional simplification is possible by the use of principal-component analysis (Vajda et al., 1985; Vlachos, 1996). However, the solution of the full-order model (or extensive data) is required to evaluate the sensitivity matrices with precision in order to ensure the accuracy of the reduced model. In addition, the achieved model order reduction decreases as we desire to retain more information. Time-scale analysis appears to be a natural framework for model order reduction of reaction systems with fast and slow reactions. The basic idea in this approach is to assume the fast dynamics to be in quasi steady state and obtain the slow dynamics subject to the corresponding quasi-steady-state constraints. In fact, the classic pseudo-steady-state hypothesis (PSSH) and partial equilibrium approximations (Peters, 1991; Williams, 1985) in essence are based on time-scale analysis arguments (Bowen et al., 1963; Fraser, 1988); however, the applicability of these approximations has been

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typically restricted to simple reaction systems and for specific regions of initial and/or operating conditions (Williams, 1985).

For complex reaction systems, the intuitive identification of independent constraints corresponding to quasi-steady-state approximations for the fast dynamics and its subsequent enforcement in the reduced-order model describing the slow dynamics are highly nontrivial. Moreover, although one may be able to identify fast and slow chemical reactions from the corresponding kinetic parameters, the species concentrations cannot in general be classified as fast or slow; mathematically stated, reaction systems exhibit multiple time-scale behavior, but their models are not in a standard singularly perturbed form (where the fast and slow states are explicitly separated) (Kumar et al., 1998). As a consequence, modelreduction methods based on singular perturbation arguments are not directly applicable to such systems. Motivated by this, past research has focused on constructing coordinate changes that allow transforming models of reaction systems into a standard singularly perturbed form. The work in Breusegem and Bastin (1991) considers isothermal reaction systems and employs a linear change of variables to obtain a standard singularly perturbed model. The work in Kumar et al. (1998) provides necessary and sufficient conditions for the existence of a nonlinear coordinate change to obtain a standard singularly perturbed model of a general class of two time-scale systems with nonexplicit time-scale separation which includes nonisothermal reaction systems. These analytical approaches explicitly identify the slow and fast variables and provide explicit reduced-order models for the slow and fast dynamics; however, the construction of the requisite coordinate changes becomes increasingly tedious as the complexity of the reaction system increases. On the other hand, numerical approaches to model reduction based on time-scale analysis have also been proposed as an alternative and applied to large reaction systems. We note the method in Maas and Pope (1992) that generates numerical lookup tables of the steady-state solutions evaluated subject to the quasi-steady-state approximation for the fast dynamics. We also note the popular approach of computational singular perturbations (CSP) (Lam and Goussis, 1994), which involves linearizing the dynamic model in each time step and applying essentially linear modal decomposition to separate the slow and fast modes. Note, however, that the inherent nonlinearity of chemical reaction systems requires a continuous update of the linearized model, and a corresponding update of the basis vector that separates the slow and fast modes of the model, hence making this approach computationally intensive. Clearly, there is a need for a general approach that retains the insights and appeal of the analytical approaches, and is (practically) applicable to reaction systems of high dimension.

In this work, we consider nonisothermal reaction systems that exhibit dynamics in two different time scales, owing to the presence of fast and slow reactions, and address the systematic derivation of reduced-order *nonlinear* models of the slow dynamics of such systems. More specifically, we initially outline a formulation of the standard material and energy balance model of such reaction systems that leads to a system of ODEs containing a small, singular perturbation parameter (the inverse of a "large" reaction rate constant). Then, within the framework of singular perturbations, we systematically identify the independent algebraic constraints that define a low-dimensional equilibrium manifold where the slow dynamics of the system are constrained to evolve. These algebraic constraints essentially correspond to "kinetically independent" reaction equilibrium or complete conversion constraints, for "stoichiometrically independent" fast reversible and irreversible reactions, respectively. A description of the slow dynamics of this system on this manifold is then obtained and is shown to be a differential algebraic equation (DAE) system of high index. The derivation of standard state-space realizations (that is, ODE descriptions) of the slow dynamics in terms of the original state variables is addressed, and insight into the nature of the slow and fast variables is provided. The various steps of the developed modeling and reduction method are illustrated throughout with the classic Michaelis-Menten reaction system. Finally, the developed method is applied to two realistic reaction systems, an ozone decomposition reaction system and a reaction mechanism for esterification of carboxylic acid.

Singular Perturbation Modeling of Fast and Slow Reaction Systems

Consider a spatially homogeneous chemical reaction system, where the following R reactions involving S species take place

$$\sum_{j=1}^{S} \nu_{ij} A_j = 0 \quad i = 1, \ldots, R, \tag{1}$$

where A_j denotes the species j and ν_{ij} denotes the stoichiometric coefficient of the species j in the reaction i. Let r_i denote the reaction rate of the reaction i (in moles per unit time per unit volume) and ΔH_i denote the heat of reaction with the usual convention of $\Delta H_i < 0$ for an exothermic reaction. In the case of constant volume of the reacting mixture, the material and energy balances describing the evolution of the species compositions and temperature take the form

$$\dot{C}_j = \sum_{i=1}^{R} \nu_{ij} r_i + \frac{F}{\rho V}\left(C_j^{\text{in}} - C_j\right) \quad j = 1, \ldots, S$$

$$\dot{T} = -\frac{1}{\rho C_p} \sum_{i=1}^{R} \Delta H_i r_i + \frac{F C_p^{\text{in}}}{\rho V C_p}(T^{\text{in}} - T) + \frac{UA}{\rho V C_p}(T^h - T), \tag{2}$$

where C_j denotes the molar concentration of species j, T denotes the temperature, V denotes the volume of the reacting mixture, F denotes the mass flow rate, T^{in} is the temperature of the inlet stream, ρ denotes the density of the reacting mixture, C_p is the mass heat capacity of the mixture, U denotes the heat-transfer coefficient, A is the area of heat transfer, and T^h denotes the temperature of the heat-transfer medium. The model of Eq. 2 can be written in matrix form as

$$\begin{bmatrix} \dot{C}_1 \\ \vdots \\ \dot{C}_j \\ \vdots \\ \dot{C}_S \\ \dot{T} \end{bmatrix} = \begin{bmatrix} \nu_{11} & \cdots & \nu_{i1} & \cdots & \nu_{R1} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ \nu_{1j} & \cdots & \nu_{ij} & \cdots & \nu_{Rj} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ \nu_{1S} & \cdots & \nu_{iS} & \cdots & \nu_{RS} \\ \dfrac{-\Delta H_1}{\rho C_p} & \cdots & \dfrac{-\Delta H_i}{\rho C_p} & \cdots & \dfrac{-\Delta H_R}{\rho C_p} \end{bmatrix} \begin{bmatrix} r_1 \\ \vdots \\ r_i \\ \vdots \\ r_R \end{bmatrix}$$

$$+ \left[\begin{pmatrix} C_1^{\text{in}} - C_1 \\ \vdots \\ C_j^{\text{in}} - C_j \\ \vdots \\ C_S^{\text{in}} - C_S \\ \dfrac{C_p^{\text{in}}}{C_p}(T^{\text{in}} - T) \end{pmatrix} \frac{F}{\rho V} + \begin{pmatrix} 0 \\ \vdots \\ 0 \\ \vdots \\ 0 \\ (T^h - T) \end{pmatrix} \frac{UA}{\rho V} \right] \tag{3}$$

or in the following general form

$$\dot{x} = \mathcal{V}\,(x) r(x) + g(x), \tag{4}$$

where $x = (C_1, C_2, \ldots, C_S, T)^T \in X \subset \mathbb{R}^n$ is the vector of state variables of dimension $n = S + 1$, $\mathcal{V}\,(x)$ is a $(n \times R)$ "generalized" stoichiometric matrix, $r(x)$ is an R-dimensional reaction rate vector, and $g(x)$ denotes an n-dimensional vector comprising terms associated with mass flow and heat transfer. The preceding form also incorporates the material and energy balance equations in other cases, too, such as gas-phase reactors operating at constant pressure. The reaction rate r_i is usually expressed as a product of a reaction rate constant, $k_i(T)$, which is typically an exponential function of temperature alone, and a nonlinear (often polynomial) function of concentrations, $\bar{r}_i(C)$, as $r_i(x) = k_i(T)\bar{r}_i(C)$, where $C = (C_1, C_2, \ldots, C_S)^T$ is the vector of concentrations. In adopting such a rate expression for each reaction i, we implicitly assume (without loss of generality) that in the case of reversible reactions, the forward and backward reactions are represented separately in Eq. 2.

It is assumed that the reactions $i = 1, \ldots, R - p$ are slow and the reactions $i = R - p + 1, \ldots, R$ are fast in the temperature range of interest (this classification can change within a broad temperature range). Specifically, it is assumed that there exists a large parameter, $k^* = k_{(R-p+1)}(T^o)$, equal to the reaction rate constant of the slowest fast reaction evaluated at some nominal temperature T^o, such that first $R - p$ reactions have rate constants of smaller order of magnitude than $k^*[k_i/k^* \ll O(1)$ for $i = 1, \ldots, R - p]$, and the remaining p reactions have rate constants of the same order of magnitude as $k^*[k_i/k^* \cong O(1)$ for $i = R - p + 1, \ldots, R]$ Table 1 contains representative orders of magnitude of rate constants that allow such a characterization, taken from Aris, (1989).

Table 1. Representative Orders of Magnitude of Rate Constants*

Classification	Reaction	Magnitude of k_i (L/mol·s) at 30°C
Fast	HCl + NaOH	10^{11}
Medium	CO_2 + NaOH	10^4
Slow	$HCOOCH_3$ + NaOH	10^1

*From *Elementary Chemical Reactor Analysis* (Aris, 1989).

This classification of reactions to fast and slow allows a partition of the righthand side of Eq. 3, as follows

$$\begin{bmatrix} \dot{C}_1 \\ \vdots \\ \dot{C}_S \\ \dot{T} \end{bmatrix} = \begin{bmatrix} \nu_{11} & \cdots & \nu_{(R-p)1} \\ \vdots & \ddots & \vdots \\ \nu_{1S} & \cdots & \nu_{(R-p)S} \\ \dfrac{-\Delta H_1}{\rho C_p} & \cdots & \dfrac{-\Delta H_R}{\rho C_p} \end{bmatrix} \begin{bmatrix} r_1 \\ \vdots \\ r_{R-p)} \end{bmatrix} + g(x)$$

$$+ \begin{bmatrix} \nu_{(R-p+1)1} & \cdots & \nu_{R1} \\ \vdots & \ddots & \vdots \\ \nu_{(R-p+1)S} & \cdots & \nu_{RS} \\ \dfrac{-\Delta H_{(R-p+1)}}{\rho C_p} & \cdots & \dfrac{-\Delta H_R}{\rho C_p} \end{bmatrix} \begin{bmatrix} r_{(R-p+1)} \\ \vdots \\ r_R \end{bmatrix} \tag{5}$$

or in general form

$$\dot{x} = \mathcal{V}_s\,(x) r_s(x) + g(x) + \mathcal{V}_f(x) r_f(x), \tag{6}$$

where the subscripts s and f denote the generalized stoichiometric matrices and the reaction rate vectors for the slow and fast reactions, respectively.

Note that the reaction rate of a fast reaction r_i is the product of a large term [k_i is of $O(k^*)$] and a small term [$\bar{r}_i$ is of $O(1/k^*)$]; the presence of such terms in the vector $r_f(x)$ introduces a stiffness in the dynamic system of Eq. 6. Assuming that the residence time of the reactor and the characteristic time constant of heat transfer are of the same order of magnitude as the slow reaction rate constants, k_i, $i = 1, \ldots, R - p$, we can combine the slow reaction terms along with the mass flow and the heat-transfer term to obtain the vector $f(x) = \mathcal{V}_s(x) r_s(x) + g(x)$, which is independent of the large parameter, k^*, and Eq. 6 can be written as

$$\dot{x} = f(x) + \mathcal{V}_f(x) r_f(x). \tag{7}$$

In order to isolate the stiffness of Eq. 7 to a single parameter, we extract the large parameter k^* from the reaction rate vector for the fast reactions, $r_f(x)$, to obtain

$$r_f(x) = k^* \text{diag}\left[\frac{k_i}{k^*}\right] \bar{r}_f(C) \quad i = R - p + 1, \ldots, R. \tag{8}$$

Observing that the diagonal matrix, diag$[k_{\text{i}}/k^*]$, comprises terms of $O(1)$, we note that the stiffness is indeed isolated to the single parameter k^*. Defining the $(R - p) \times (R - p)$ diagonal matrix $K_f(T)$,

$$K_f(T) = \mathrm{diag}\left[\frac{k_i}{k^*}\right] \quad i = R - p + 1, \ldots, R, \tag{9}$$

which comprises the "scaled" reaction rate constants of the fast reactions, and also defining the small parameter, $\epsilon = 1/k^*$, we obtain the following ODE system with a small parameter that describes the system dynamics

$$\dot{x} = f(x) + \frac{1}{\epsilon}\mathcal{V}_f(x) K_f(T) \bar{r}_f(C). \tag{10}$$

Before proceeding with the identification and characterization of the low-dimensional equilibrium manifold where the slow dynamics of the reaction system evolves and the subsequent derivation of reduced-order models on this manifold, we illustrate the preceding modeling framework with the classic Michaelis-Menten reaction system (Bailey and Ollis, 1977; Breusegem and Bastin, 1991).

Example 1. We consider the Michaelis-Menten reaction system, which consists of the following three reactions, in an isothermal batch reactor

$$\begin{aligned} A + B &\xrightarrow{k_1} C \\ C &\xrightarrow{k_2} A + B \\ C &\xrightarrow{k_3} B + D, \end{aligned} \tag{11}$$

where A represents the substrate, B denotes the enzyme, C represents the enzyme–substrate complex and D denotes the product. The reaction rates for these reactions are given by $r_1 = k_1 C_A C_B$, $r_2 = k_2 C_C$, and $r_3 = k_3 C_C$, respectively. The values of the reaction rate constants are $k_1 = 110$, $k_2 = 100$, $k_3 = 1$ in consistent units. The dynamic model can be readily expressed in the matrix form of Eq. 3 as

$$\begin{bmatrix} \dot{C}_A \\ \dot{C}_B \\ \dot{C}_C \\ \dot{C}_D \end{bmatrix} = \begin{bmatrix} -1 & 1 & 0 \\ -1 & 1 & 1 \\ 1 & -1 & -1 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix}. \tag{12}$$

Clearly, the first and the second reactions are faster than the third reaction, based on their reaction rate constants ($k_1 \gg k_3$ and $k_2 \gg k_3$). Defining the small parameter $\epsilon = 1/k^* = 1/k_2$, the system of Eq. 12 can be readily transformed to the form of Eq. 10 as

$$\begin{bmatrix} \dot{C}_A \\ \dot{C}_B \\ \dot{C}_C \\ \dot{C}_D \end{bmatrix} = \begin{bmatrix} 0 \\ r_3 \\ -r_3 \\ r_3 \end{bmatrix} + \frac{1}{\epsilon} \begin{bmatrix} -1 & 1 \\ -1 & 1 \\ 1 & -1 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} k_1' & 0 \\ 0 & k_2' \end{bmatrix} \begin{bmatrix} \bar{r}_1 \\ \bar{r}_2 \end{bmatrix}, \tag{13}$$

where $k_1' = (k_1/k^*)$, $k_2' = (k_2/k^*)$, $\bar{r}_1 = C_A C_B$ and $\bar{r}_2 = C_C$.

Equilibrium Manifold

In this section, we address the identification and characterization of the equilibrium manifold for the fast dynamics, which is also the manifold where the slow dynamics of the reaction system evolves. To this end, we initially assume that:

(1) the stoichiometric vectors of the fast reactions are linearly independent.

The *stoichiometric linear independence* of the fast reactions is equivalent to the generalized stoichiometric matrix for the fast reactions $\mathcal{V}_f(x)$ having full column rank p. If the column rank of $\mathcal{V}_f(x)$ is $p' < p$, we can construct a matrix $\mathcal{V}_f'(x)$ of dimension $(n \times p')$ with full column rank p', by selecting p' independent columns of matrix $\mathcal{V}_f(x)$. Then Eq. 10 can be written as

$$\dot{x} = f(x) + \frac{1}{\epsilon}\mathcal{V}_f'(x) \bar{r}_f'(x), \tag{14}$$

with a modified $(p' \times 1)$ reaction rate vector

$$\bar{r}_f'(x) = \left\{ \left[\mathcal{V}_f'(x)\right]^T \left[\mathcal{V}_f'(x)\right] \right\}^{-1} \left[\mathcal{V}_f'(x)\right]^T \times \left[\mathcal{V}_f(x)\right] K_f(T) \bar{r}_f(C). \tag{15}$$

The vector $\bar{r}_f'(x)$ contains the scaled reaction rates for the stoichiometrically independent fast reactions, and is a function of both temperature and concentrations. If the matrix $\mathcal{V}_f(x)$ has full column rank to begin with, then $\mathcal{V}_f'(x) = \mathcal{V}_f(x)$ and $\bar{r}_f'(x) = K_f(T)\bar{r}_f(C)$ in Eq. 14.

Example 1 (Continued). For the Michaelis-Menten reaction system examined earlier, the corresponding stoichiometric matrix for the fast reactions is

$$\mathcal{V}_f(x) = \begin{bmatrix} -1 & 1 \\ -1 & 1 \\ 1 & -1 \\ 0 & 0 \end{bmatrix}.$$

Clearly, $\mathcal{V}_f(x)$ has a rank deficiency [rank $(\mathcal{V}_f(x)] = 1$), as the stoichiometric vectors of the two fast reactions are linearly dependent. Selecting the first column of $\mathcal{V}_f(x)$, we can form a new stoichiometric matrix $\mathcal{V}_f'(x) = [-1 \quad -1 \quad 1 \quad 0]^T$, which has full column rank, with a "scaled" reaction rate

$$\begin{aligned} \bar{r}_f'(x) &= \frac{1}{k^*}\left[k_1(T)\bar{r}_1(C) - k_2(T)\bar{r}_2(C)\right] \\ &= \frac{k_1(T)}{k^*}\left[\bar{r}_1(C) - \frac{\bar{r}_2(C)}{\kappa(T)}\right], \end{aligned}$$

where $\kappa(T) = [k_1(T)/k_2(T)]$ represents the reaction equilibrium constant. Observe that the reaction rate $\bar{r}_f'(x)$ represents the scaled net forward reaction rate for the fast reversible reaction $A + B \rightleftharpoons C$.

Remark 1. Note that in the case of a reversible reaction where both the forward and backward reactions are fast and the two reactions are obviously dependent, the operations just described lead to a reaction rate $\bar{r}_f'(x)$ that is the scaled net forward reaction rate of the reversible reaction, as illustrated in Example 1.

Let us now consider the fast dynamics of Eq. 14. Defining a "stretched" fast time scale $\tau = t/\epsilon$, the system of Eq. 14 takes the form

$$\frac{dx}{d\tau} = \epsilon f(x) + \mathcal{V}_f'(x)\bar{r}_f'(x). \tag{16}$$

In the limit $\epsilon \to 0$, we obtain the description of the fast dynamics of the system as

$$\frac{dx}{d\tau} = \mathcal{V}_f'(x)\bar{r}_f'(x). \tag{17}$$

Given the full column rank of $\mathcal{V}_f'(x)$, the (quasi-) steady-state constraints for this system take the form

$$0 = \bar{r}_f'(x). \tag{18}$$

Proposition 1. Consider the system in Eq. 14, with $\mathcal{V}_f'(x)$ having full column rank p'. Then

$$\operatorname{rank}\left(\frac{\partial \bar{r}_f'(x)}{\partial x}\right) < n.$$

Proof. Note that the number of independent reactions $\mathcal{R}$ in the reaction system of Eq. 14 satisfies

$$\mathcal{R} \leq S - \operatorname{rank}(\mathcal{E}), \tag{19}$$

where $\mathcal{E}$ denotes the element matrix (Aris, 1989; Maas and Pope, 1992). The fact that at least one element must be present in a reactive system implies that rank $(\mathcal{E}) \geq 1$, which implies that $\mathcal{R} < \mathcal{S}$. Note that the dimension of the vector $\bar{r}_f'(x)$ is less than or equal to $\mathcal{R}$ (where the equality corresponds to all independent reactions being fast). This indicates that the vector $\bar{r}_f'(x)$ is of dimension $p' < n$, which implies that

$$\operatorname{rank}\left(\frac{\partial \bar{r}_f'(x)}{\partial x}\right) < n. \tag{20}$$

The result of Proposition 1 establishes that the condition of Eq. 18 does not specify *isolated equilibrium points* for the dynamic system of Eq. 17 (as one cannot obtain a solution for x); instead, it specifies an *equilibrium manifold*, $\mathcal{M} = \{x \in X: \bar{r}_f'(x) = 0\}$, where also the slow dynamics is constrained to evolve. The algebraic constraints $\bar{r}_f'(x) = 0$, defining this manifold comprise of "classic" quasi-steady-state conditions of complete conversion for irreversible reactions and reaction equilibrium for reversible ones.

We can now proceed to characterize the dimension of the manifold $\mathcal{M}$, beginning with ensuring that there is no potential redundancy in the algebraic equations in Eq. 18. To this end, we assume that:

(2) the scalar functions comprising the scaled reaction rates of the fast reactions, $\bar{r}_f'(x)$, are functionally independent on the manifold $\mathcal{M}$, that is, their gradient covector fields are linearly independent.

This amounts to the Jacobian of the vector $\bar{r}_f'(x)$, that is, $\{[\partial \bar{r}_f'(x)]/\partial x\}$, having full row rank p' on $\mathcal{M}$ and can be viewed as a *"kinetic" linear independence* of the fast reactions. If it holds, it specifies the upper bound on the dimension of the manifold $\mathcal{M}$ as $n - p'$. If, on the other hand, there are only $p^* < p'$ independent constraints, that is, the row rank of $[\partial \bar{r}_f'(x)/\partial x]$ is $p^* < p'$, then there exists a $p' \times p'$ dimensional nonsingular matrix $E(x)$, such that $\bar{r}_f^*(x) = E(x)\bar{r}_f'(x)$ has the first p^* rows with independent scalar functions, and the last $p' - p^*$ rows identically equal to 0. This results in a transformed stoichiometric matrix $\mathcal{V}_f^*(x) = \mathcal{V}_f'(x)E(x)^{-1}$, whose last $p' - p^*$ columns can be discarded along with the last $p' - p^*$ rows of $\bar{r}_f^*(x)$; the system of Eq. 14 can then be written as

$$\dot{x} = f(x) + \frac{1}{\epsilon}\mathcal{V}_f^*(x)\bar{r}_f^*(x), \tag{21}$$

where $\bar{r}_f^*(x)$ is a $(p^* \times 1)$ vector of *kinetically independent* scaled reaction rates, and $\mathcal{V}_f^*(x)$ is an $(n \times p^*)$ matrix of *stoichiometrically independent* fast reactions. In this case, the upper bound on the dimension of the manifold $\mathcal{M}$ is $n - p^*$.

Example 2. Consider a hypothetical system that includes two fast irreversible reactions, $A \to C$ and $A + B \to D$. The nonlinear functions describing the scaled reaction rates of the two fast reactions are $\bar{r}_1'(x) = k_1'C_A$ and $\bar{r}_2'(x) = k_2'C_AC_B$, and $k_1' = (k_1/k^*)$ and $k_2' = (k_2/k^*)$. The low-dimensional manifold is defined by the algebraic constraints $\bar{r}_1'(x) = k_1'C_A = 0$ and $\bar{r}_2'(x) = k_2'C_AC_B = 0$. The Jacobian $[\partial \bar{r}_f'(x)/\partial x]$, of the vector $\bar{r}_f'(x)$ can be readily obtained as

$$\left[\partial \bar{r}_f'(x)/\partial x\right] = \begin{bmatrix} k_1' & 0 & 0 & 0 \\ k_2'C_B & k_2'C_A & 0 & 0 \end{bmatrix}.$$

Clearly, the Jacobian of the vector $\bar{r}_f'(x)$ has rank 1 for $C_A = 0$. We construct a 2×2 nonsingular matrix $E(x)$ as

$$E(x) = \begin{bmatrix} \dfrac{1}{k_1'} & 0 \\ \dfrac{C_B}{k_1'} & \dfrac{-1}{k_2'} \end{bmatrix},$$

such that $\bar{r}_f^*(x) = [C_A \quad 0]^T$ has the last row $(p - p^* = 2 - 1 = 1)$ identically equal to 0, and the stoichiometric matrix $\mathcal{V}_f^*(x)$ is given by

$$\mathcal{V}_f^*(x) = \begin{bmatrix} -1 & -1 \\ 0 & -1 \\ 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} k_1' & 0 \\ k_2'C_B & -k_2' \end{bmatrix} = \begin{bmatrix} -k_1' - k_2'C_B & * \\ -k_2'C_B & * \\ k_1' & * \\ k_2'C_B & * \end{bmatrix}.$$

Observe that only the first column $(p^* = 1)$ of $\mathcal{V}_f^*(x)$ is useful, as the last row of $\bar{r}_f^*(x)$ is identically equal to 0.

In what follows, for notational simplicity the prime and asterisk superscripts are dropped, and the system of Eq. 21 is expressed as

$$\dot{x} = f(x) + \frac{1}{\epsilon}\mathcal{V}_f(x)\bar{r}_f(x), \qquad (22)$$

where the *stoichiometric linear independence* and *kinetic linear independence* are assumed to hold. We stress that this is essential for obtaining the maximal set of independent algebraic constraints that specify the equilibrium manifold.

Nonlinear Reduced-Order Model

We can now proceed with the derivation of the reduced-order model that describes the slow dynamics of the system

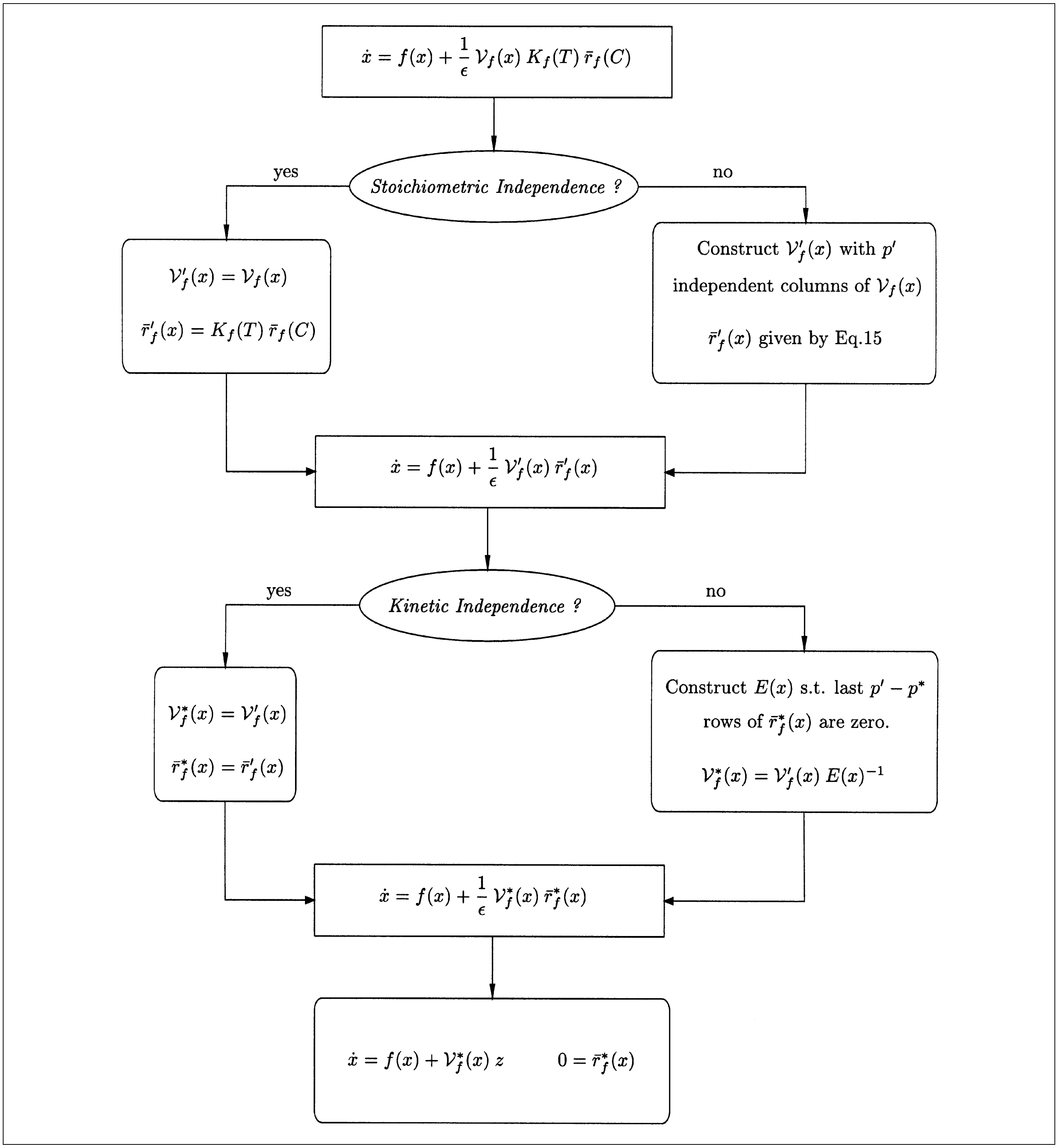

Figure 1. Model reduction algorithm for two time-scale reaction systems.

of Eq. 22. Note that the quasi-steady-state constraints $\bar{r}_f(x) = 0$ must be satisfied in the slow time scale. In addition, referring to the system of Eq. 22, in the limit $\epsilon \to 0$, the term $(1/\epsilon)[\bar{r}_f(x)]$ becomes indeterminate. More specifically, for a fast reaction i, the reaction rate r_i is

$$r_i = k_i \bar{r}_i = \left(\frac{k_i}{k^*}\right) k^* \bar{r}_i = \left(\frac{k_i}{k^*}\right)\left(\frac{\bar{r}_i}{\epsilon}\right), \tag{23}$$

where $k^* = 1/\epsilon$ represents a large term (of $O(1/\epsilon)$), $\bar{r}_i$ is a small term (of $O(\epsilon)$), and $(k_i/k^*) \cong O(1)$. In the limit as $\epsilon \to 0$, the large term $1/\epsilon = k^* \to \infty$ and the small term $\bar{r}_i \to 0$, rendering the product r_i (reaction rate of the fast reaction i) indeterminate. This corresponds to the fact that in the limit as the large parameter $k^* = 1/\epsilon$, representative of large reaction rate constants in the reaction rate expressions, approaches infinity, the independent fast reactions approach the quasi-steady-state conditions (that is, partial equilibrium for reversible reactions and complete conversion for irreversible reactions) specified by $\bar{r}_f(x) = 0$, and the corresponding reaction rates cannot be evaluated from the kinetic rate expressions $r_f(x)$. Let $z = \lim_{\epsilon \to 0} \{[\bar{r}_f(x)]/\epsilon\}$ denote the vector of indeterminate (but finite) reaction rates of the independent fast reactions in the slow time scale. Then the slow dynamics of the system in Eq. 22 is described by the following system

$$\begin{aligned} \dot{x} &= f(x) + \mathcal{V}_f(x) z \\ 0 &= \bar{r}_f(x). \end{aligned} \tag{24}$$

The developed method so far can be summarized in the algorithm shown in Figure 1.

Note that the algebraic equations in Eq. 24 are singular in the variables z. As a result, although these variables change with time, there is no explicit expression for their calculation; instead, they are implicitly specified by the algebraic constraints. This indicates that the differential algebraic equation (DAE) system of Eq. 24 has a high index (Kumar and Daoutidis, 1999), and the constraints need to be differentiated a sufficient number of times to obtain a solution for the variables z. One differentiation with respect to time yields

$$\frac{d\bar{r}_f(x)}{dt} = L_f \bar{r}_f(x) + L_{\mathcal{V}_f} \bar{r}_f(x) z = 0, \tag{24}$$

where $L_{\mathcal{V}_f}\bar{r}_f(x)$ denotes the matrix whose (i,j)th component is the standard Lie (directional) derivative $L_{\mathcal{V}_{f_j}}\bar{r}_{f_i}(x) = [\partial \bar{r}_{f_i}(x)/\partial x]\mathcal{V}_{f_j}$, where $\mathcal{V}_{f_j}$ is the jth column of $\mathcal{V}_f(x)$ and $\bar{r}_{f_i}$ is the ith component of $\bar{r}_f(x)$; and $L_f \bar{r}_f(x)$ denotes the p-dimensional row vector whose ith element is the Lie derivative $L_f \bar{r}_{f_i}(x)$. If $L_{\mathcal{V}_f}\bar{r}_f(x)$ is singular, then $L_f \bar{r}_f(x) = 0$ constitutes additional constraints, indicative of the existence of a lower-dimensional manifold where the variables x are constrained to evolve. On the other hand, if $L_{\mathcal{V}_f}\bar{r}_f(x)$ is nonsingular, then the algebraic variables z can be solved from Eq. 25, indicating that the index of the DAE system is two. This also fixes the dimension of the manifold where x is constrained to evolve at $n - p$, and the p algebraic constraints ($\bar{r}_f(x) = 0$) completely define this manifold.

The general structure of the $(p \times p)$ matrix $L_{\mathcal{V}_{\bar{f}}} r_f(x)$ has the form

$$L_{\mathcal{V}_f}\bar{r}_f(x) = \begin{bmatrix} L_{\mathcal{V}_{f_1}}\bar{r}_{f_1} & \cdots & L_{\mathcal{V}_{f_1}}\bar{r}_{f_j} & \cdots & L_{\mathcal{V}_{f_1}}\bar{r}_{f_p} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ L_{\mathcal{V}_{f_k}}\bar{r}_{f_1} & \cdots & L_{\mathcal{V}_{f_k}}\bar{r}_{f_j} & \cdots & L_{\mathcal{V}_{f_k}}\bar{r}_{f_p} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ L_{\mathcal{V}_{f_p}}\bar{r}_{f_1} & \cdots & L_{\mathcal{V}_{f_p}}\bar{r}_{f_j} & \cdots & L_{\mathcal{V}_{f_p}}\bar{r}_{f_p} \end{bmatrix}, \tag{26}$$

where $L_{\mathcal{V}_{f_k}}\bar{r}_{f_j}$ denotes

$$L_{\mathcal{V}_{f_k}}\bar{r}_{f_j} = \sum_{l=1}^{S} \left(\frac{\partial \bar{r}_{f_j}(x)}{\partial x_l}\right)\nu_{kl} + \left(\frac{\partial \bar{r}_{f_j}(x)}{\partial T}\right)\left(\frac{-\Delta H_k}{\rho C_p}\right),$$

where $\mathcal{V}_{f_k}$ represents the kth stoichiometric vector and is given by

$$\mathcal{V}_{f_k} = \left[\nu_{k1}, \ldots, \nu_{kl}, \ldots, \nu_{kS}, \frac{-\Delta H_k}{\rho C_p}\right]^T,$$

and the jth row in the Jacobian of the vector $\bar{r}_f(x)$ corresponding to the jth constraint $\bar{r}_{f_j}(x)$ is given by

$$\frac{\partial \bar{r}_{f_j}(x)}{\partial x} = \left[\frac{\partial \bar{r}_{f_j}(x)}{\partial x_1}, \ldots, \frac{\partial \bar{r}_{f_j}(x)}{\partial x_l}, \ldots, \frac{\partial \bar{r}_{f_j}(x)}{\partial x_S}, \frac{\partial \bar{r}_{f_j}(x)}{\partial T}\right].$$

Note that in an arbitrary reaction system of S species and R reactions, the structure of the matrix $L_{\mathcal{V}_f}\bar{r}_f(x)$ can range from a diagonal matrix to a completely full matrix, rendering a general analysis of the nonsingularity of this matrix difficult. Such an analysis can be carried out for some special cases, for example, the case of a single constraint corresponding to reaction equilibrium or complete conversion, or multiple constraints that, however, do not involve common reactants (see Vora, 2000), and does indeed verify that the matrix $L_{\mathcal{V}_f}\bar{r}_f(x)$ is nonsingular. Motivated by this, we will assume in what follows that $L_{\mathcal{V}_f}\bar{r}_f(x)$ is nonsingular, which ensures that the index of DAE system of Eq. 24 is two. A state-space realization of the DAE system of Eq. 24, which describes the evolution of the slow dynamics of the reaction system of Eq. 10, on the manifold $\mathfrak{M}$, is given in the following proposition (its proof is rather straightforward and is omitted for brevity).

Proposition 2. Consider the DAE system of Eq. 24. Assuming that the $(p \times p)$ matrix $L_{\mathcal{V}_f}\bar{r}_f(x)$ is nonsingular, the system:

$$\dot{x} = f(x) - \mathcal{V}_f(x)\left(L_{\mathcal{V}_f}\bar{r}_f(x)\right)^{-1}\left(L_f \bar{r}_f(x)\right), \tag{27}$$

where $x \in \mathfrak{M} = \{x \in X : 0 = \bar{r}_f(x)\}$, is a state-space realization of Eq. 24.

Example 1 (continued). For the Michaelis-Menten reaction system, the algebraic variable z can be readily evaluated as

$$z = \frac{(\kappa C_A + 1)(k_3 \kappa C_A C_B)}{\kappa(C_A + C_B) + 1}, \tag{28}$$

where $\kappa = (k_1/k_2) = (k_1'/k_2')$ represents the reaction equilibrium constant for the reversible reaction $A + B \rightleftharpoons C$. The state-space realization of the slow dynamics according to Proposition 1 is derived as

$$\begin{bmatrix} \dot{C}_A \\ \dot{C}_B \\ \dot{C}_C \\ \dot{C}_D \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ -1 \\ 1 \end{bmatrix} [k_3 C_C] + \begin{bmatrix} -1 \\ -1 \\ 1 \\ 0 \end{bmatrix} \left[\frac{(\kappa C_A + 1)(k_3 C_C)}{\kappa (C_A + C_B) + 1} \right]$$

$$0 = k_1' C_A C_B - k_2' C_C. \tag{29}$$

Note that the state-space realization of Eq. 27 is not of minimal order, as x evolves in an $(n-p)$-dimensional manifold. An $(n-p)$-dimensional realization can be obtained in appropriately transformed coordinates. Specifically, given the p-dimensional vector field $\bar{r}_f(x)$, one can always find a vector field $\phi(x)$ of dimension $(n-p)$ such that

$$\begin{bmatrix} \zeta \\ \eta \end{bmatrix} = T(x) = \begin{bmatrix} \phi(x) \\ \bar{r}_f(x) \end{bmatrix} \tag{30}$$

is a valid coordinate transformation. In these coordinates the constraints $\bar{r}_f(x) = 0$ reduce to $\eta = 0$, which allows deriving the reduced-order state-space realization given in Proposition 3.

Proposition 3. Consider the DAE system of Eq. 24, where the matrix $L_{\mathcal{V}_f} \bar{r}_f(x)$ is nonsingular. Then the dynamic system:

$$\dot{\zeta} = L_f \phi(x)|_{x = T^{-1}(\zeta, 0)}$$

$$- \left\{ L_{\mathcal{V}_f} \phi(x) \left[L_{\mathcal{V}_f} \bar{r}_f(x) \right]^{-1} \left[L_f \bar{r}_f(x) \right] \right\}_{x = T^{-1}(\zeta, 0)} \tag{31}$$

is a state-space realization of this system of dimension $(n-p)$.

In the coordinate change of Eq. 30, the slow variables $\zeta = \phi(x)$ can be chosen with considerable freedom. The simplest choice is to use a proper subset $x_1, \ldots, x_{(n-p)}$ of the original state variables x. This leads to a reduced-order model in terms of original state variables, and hence retains the physical significance of the state variables. Note that these variables cannot be strictly treated as the "true" slow variables of the system (recall the nonexplicit separation of fast and slow variables in the original model); they will, in general, exhibit fast transients too, as their initial conditions may be away from the equilibrium manifold. In order to simulate the slow dynamics in this case, we would need to initialize the model of Eq. 31 "sufficiently close" to the manifold $\mathfrak{M}$, that is, with $x_1(0^+), \ldots, x_{(n-p)}(0^+)$ such that $\bar{r}_f[x(0^+)] \cong O(\epsilon)$. In practices, this can be achieved by integrating the (nonstiff) fast dynamics (see Eq. 17) for a small time t^* [of $O(\epsilon)$], checking that the variables of interest satisfy the constraints within a desired approximation, and initializing the model of the slow dynamics from these values.

Note that it is in principle possible to obtain true slow variables that do not exhibit fast transients. These variables correspond to a choice of $\zeta = \phi(x)$ such that $L_{\mathcal{V}_f} \phi(x) \equiv 0$, which decouples the slow dynamics from the evolution of the fast variables η. In this case, the dynamic system of Eq. 31 simplifies to

$$\dot{\zeta} = L_f \phi(x)|_{x = T^{-1}(\zeta, 0)} \tag{32}$$

and the initial condition for the reduced-order model is obtained directly from $\zeta(0) = \phi[x(0)]$. Such a transformation is possible, however, if and only if the p-dimensional distribution spanned by the columns of $\mathcal{V}_f$ is involutive (Kumar et al., 1998). The condition of involutivity of the matrix $\mathcal{V}_f$ is quite restrictive for general nonlinear systems (except for the case where $p = 1$). In contrast, the reduced-order model of Eq. 24 in terms of the original state variables can be readily used for general nonisothermal reaction systems. Furthermore, the choice of the original state variables necessitates explicit calculations of the reaction rates of the independent fast reactions in the slow time scale, which can provide valuable insight into the behavior of complex reaction systems.

Remark 2. The condition of involutivity of the distribution spanned by the columns of the generalized stoichiometric matrix for fast reactions, $\mathcal{V}_f(x)$, is trivially satisfied for an isothermal reaction system, as the condition trivially holds if $\mathcal{V}_f(x)$ is independent of state variables x. Hence, for isothermal reaction systems the true slow variables $\zeta = \phi(x)$ can be obtained by selecting $\phi(x)$ as a linear combination of x, $\phi(x) = \Phi x$, where Φ belongs to the null space of $\mathcal{V}_f(x)^T$. In this case, the initial condition for the reduced-order model is given directly by $\zeta(0) = \Phi x(0)$.

Example 1 (continued). For the Michaelis-Menten reaction system, the simplest possible transformation is to choose $\zeta = \phi(x) = [C_A C_B C_D]^T$. According to Proposition 2, the state-space realization of dimension 3 is derived as

$$\begin{bmatrix} \dot{C}_A \\ \dot{C}_B \\ \dot{C}_D \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ 1 \end{bmatrix} [k_3 \kappa C_A C_B] + \begin{bmatrix} -1 \\ -1 \\ 0 \end{bmatrix} \left[\frac{(\kappa C_A + 1)(k_3 \kappa C_A C_B)}{\kappa (C_A + C_B) + 1} \right]$$

$$C_C = \kappa C_A C_B. \tag{33}$$

Furthermore, note that for this reaction system, the distribution spanned by the columns of $\mathcal{V}_f$ is involutive (see Remark 2). The coordinates

$$\begin{bmatrix} \zeta_1 \\ \zeta_2 \\ \zeta_3 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ -1 & 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} C_A \\ C_B \\ C_C \\ C_D \end{bmatrix} \tag{34}$$

represent the true slow variables of the system. Note that these slow variables are exactly the same as those obtained in Breusegem and Bastin (1991), but the approach here is considerably simpler. The state-space realization according to Eq.

32 can be readily derived as

$$\begin{bmatrix} \dot{\zeta}_1 \\ \dot{\zeta}_2 \\ \dot{\zeta}_3 \end{bmatrix} = \begin{bmatrix} 1 \\ -1 \\ 1 \end{bmatrix} \gamma(\zeta_2, \zeta_3), \tag{35}$$

where $\gamma(\zeta_2, \zeta_3)$ denotes the reaction rate of the slow reaction in the transformed coordinates and is similar to the one in Breusegem and Bastin (1991).

Application

In this section, we apply the modeling and analysis framework presented to two chemical reaction systems, highlighting in particular how classic assumptions such as reaction equilibrium for fast reactions or pseudo-steady-state hypothesis for very reactive species arise naturally from the proposed framework. Initially we study the ozone decomposition reaction system, and demonstrate how the proposed framework encompasses various reduced models obtained by classic approximations valid under different initial and/or operating conditions. We follow this with the study of esterification of carboxylic acid reaction kinetics, and demonstrate the applicability of the proposed methodology to cases where the kinetic data for all reactions in the detailed reaction mechanism are not known.

Ozone decomposition reaction system

We consider a nonisothermal batch reactor with the ozone decomposition (see Table 2) taking place at one standard atmosphere (Petzold and Zhu, 1999). The reaction system comprises six reactions, and the reaction rate r_i for the ith reaction is given as $r_i = k_i(T)\bar{r}_i(C)$, where the reaction rate constant k_i is given by a modified Arrhenius equation, $k_i = k_i^o T^{\beta_i} \exp[-(E_i/RT)]$, and $\bar{r}_i(C)$ is expressed as the product of the reactant concentrations. The reaction rate constant data shown in Table 2 are in SI units; specifically, the activation energy E is expressed in KJ/mol, and the preexponential factor k^o is expressed in mole-m-s-K. The enthalpy and specific heat capacity data are obtained from Kee et al. (1989). The system is studied in the temperature range of 400–1000 K, for which the reaction rate constant of Reactions 4 and 6 is very small (specifically, at $T = 1{,}000$ K, $k_1 = 6.11 \times 10^{03}$, $k_2 = 3.18 \times 10^{01}$, $k_3 = 1.14 \times 10^{06}$, $k_4 = 1.25 \times 10^{-15}$, $k_5 = 1.16 \times 10^{03}$, and $k_6 = 3.14 \times 10^{-16}$), and hence these reactions are neglected. This results in a full-order model comprising material and energy balances as follows

$$\begin{bmatrix} \dot{N}_O \\ \dot{N}_{O_2} \\ \dot{N}_{O_3} \\ \dot{T} \end{bmatrix} = \begin{bmatrix} 1 & -1 & -1 & -2 \\ 1 & -1 & 2 & 1 \\ -1 & 1 & -1 & 0 \\ \dfrac{-\Delta H_1}{NC_p} & \dfrac{-\Delta H_2}{NC_p} & \dfrac{-\Delta H_3}{NC_p} & \dfrac{-\Delta H_5}{NC_p} \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \\ r_3 \\ r_5 \end{bmatrix} V, \tag{36}$$

where the subscripts O, O_2, and O_3 refer to species, the subscripts 1, 2, 3, and 5 refer to respective reactions, N_j denotes moles of species j, and $N = \Sigma_{j=1}^{3} N_j$ represents the total moles in the reactor, V is the reactor volume determined by the ideal gas law, T represents the temperature, C_p denotes the average specific heat capacity of the mixture, and ΔH_i denotes the heat of reaction for the ith reaction.

Table 2. Reaction Mechanism of the Ozone Decomposition System

No. (R_i)	Reaction	k^0	β	E
1	$O_3 + M \rightarrow O_2 + O + M$	4.31×10^{08}	0.0	92.79
2	$O_2 + O + M \rightarrow O_3 + M$	1.20×10^{01}	0.0	−8.11
3	$O_3 + O \rightarrow O_2 + O_2$	1.14×10^{07}	0.0	19.12
4	$O_2 + O_2 \rightarrow O_3 + O$	1.51×10^{07}	0.0	420.69
5	$O + O + M \rightarrow O_2 + M$	6.98×10^{06}	−1.0	1.42
6	$O_2 + M \rightarrow O + O + M$	3.80×10^{13}	−1.0	496.61

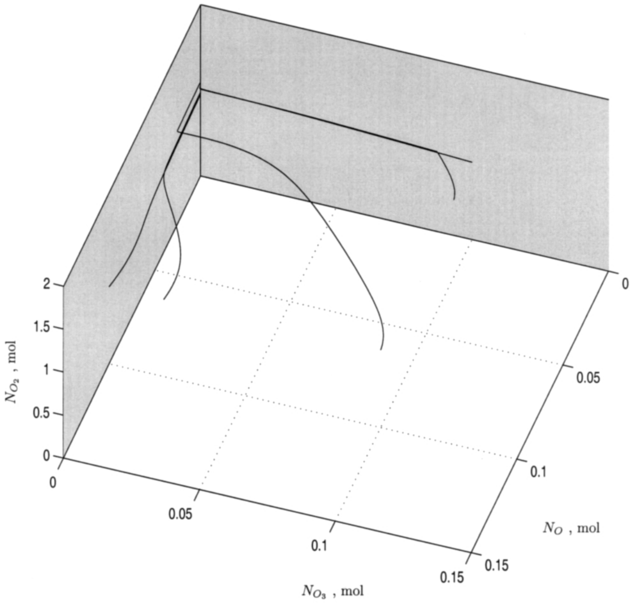

Figure 2. O_2 profile for differential initial conditions.

Figures 2 and 3 show the N_{O_2} and T profiles plotted against N_{O_3} and N_O for several different initial conditions. The trajectories shown represent the evolution of the state variables (N_{O_2}, N_{O_3}, and N_O in Figure 2 and T, N_{O_3} and N_O in Figure 3) with time obtained by simulating the full order model in Eq. 36. Observe that for the negligible amount of species O (or species O_3) present at the beginning, the classic pseudo-steady-state hypothesis for species O (or for species O_3) is easy to identify and apply. The pseudo-steady-state hypothesis for species O (or for species O_3) corresponds to the condition of $N_O = 0$ (or $N_{O_3} = 0$), and the corresponding regions in the state space are shown by the shaded planes in Figures 2 and 3. Note, however, that for similar amounts of O and O_3 present in the system at the beginning, it is difficult to predict which approximation ($N_O = 0$ or $N_{O_3} = 0$) will be valid. Specifically, observe the trajectory at the center in Figures 2 and 3; starting with an equal amount of O and O_3 ($N_O = N_{O_3} = 0.1$), the initial gradient suggests $N_O = 0$ to be the valid constraint; however, $N_{O_3} = 0$ is the valid constraint for this initial condition. Such changes in the trajectories are due to

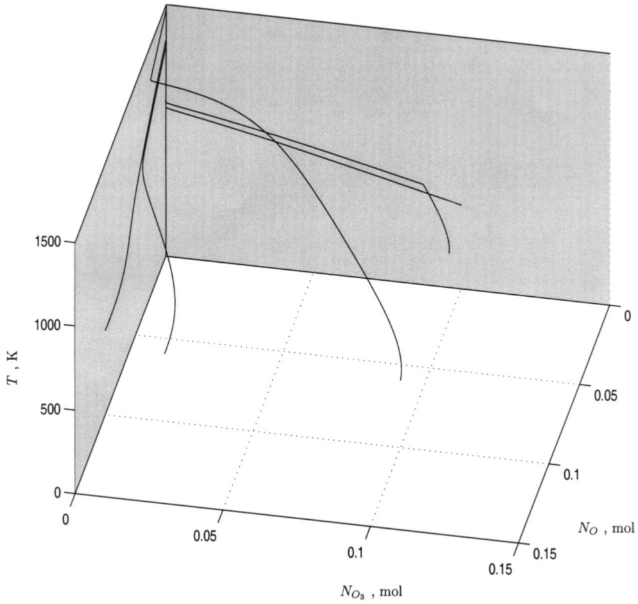

Figure 3. *T* profile for different initial conditions.

the inherent nonlinearities of the reaction system, which makes an intuitive analysis difficult for different initial and/or operating conditions. This dependence on the initial conditions is a well-known limitation of such classic approximations (Williams, 1985; Lam and Goussis, 1994), and the proposed reduction method ties these different classic approximations under one unifying framework for all feasible initial conditions, as is illustrated later.

Remark 3. For the ozone decomposition reaction system, observe that for the pseudo-steady-state hypothesis for the species O (that is, $N_O = 0$), we obtain $2O_3 \rightarrow 3O_2$ as the overall reaction; whereas for the pseudo-steady-state hypothesis for the species O_3 (that is, $N_{O_3} = 0$), we obtain $2O \rightarrow O_2$ as the overall reaction.

As can be seen, Reaction 3 is fast, whereas reactions 1, 2, and 5 are slow. Defining $k^* = k_3(T^o) = 1/\epsilon$, the system of Eq. 36 can be written in the form of Eq. 10 as

$$\begin{bmatrix}\dot{N}_O\\ \dot{N}_{O_2}\\ \dot{N}_{O_3}\\ \dot{T}\end{bmatrix} = \begin{bmatrix} 1 & -1 & -2\\ 1 & -1 & 1\\ -1 & 1 & 0\\ \dfrac{-\Delta H_1}{NC_p} & \dfrac{-\Delta H_2}{NC_p} & \dfrac{-\Delta H_5}{NC_p}\end{bmatrix}\begin{bmatrix} r_1\\ r_2\\ r_5\end{bmatrix}V + \frac{1}{\epsilon}\begin{bmatrix}-1\\ 2\\ -1\\ \dfrac{-\Delta H_3}{NC_p}\end{bmatrix}[\bar{r}_3]V. \tag{37}$$

Clearly, the conditions of stoichiometric and kinetic linear independence are satisfied, and we obtain $\bar{r}_f = \bar{r}_3 = N_O N_{O_3} = 0$ as the constraint. Defining $z = \lim_{\epsilon \rightarrow 0}(\bar{r}_3/\epsilon)$ as the variable representing the reaction rate of the fast reaction in the slow time scale, the slow dynamics of the system is obtained as a DAE system similar to Eq. 24. Differentiating the constraint $\bar{r}_3 = N_O N_{O_3} = 0$ once, we readily obtain the solution for z as:

$$z = \frac{N_{O_3}(r_1 - r_2 - 2r_5) + N_O(-r_1 + r_2)}{N_{O_3} + N_O}. \tag{38}$$

This allows eliminating z and obtaining a state-space realization of the slow dynamics as

$$\begin{bmatrix}\dot{N}_O\\ \dot{N}_{O_2}\\ \dot{N}_{O_3}\\ \dot{T}\end{bmatrix} = \begin{bmatrix} 1 & -1 & -2\\ 1 & -1 & 1\\ -1 & 1 & 0\\ \dfrac{-\Delta H_1}{NC_p} & \dfrac{-\Delta H_2}{NC_p} & \dfrac{-\Delta H_5}{NC_p}\end{bmatrix}\begin{bmatrix} r_1\\ r_2\\ r_5\end{bmatrix}V + \begin{bmatrix}-1\\ 2\\ -1\\ \dfrac{-\Delta H_3}{NC_p}\end{bmatrix}\left[\frac{N_{O_3}(r_1 - r_2 - 2r_5) + N_O(-r_1 + r_2)}{N_{O_3} + N_O}\right]V. \tag{39}$$

Remark 4. Note that the constraint $\bar{r}_f = \bar{r}_3 = \mathrm{N}_O \mathrm{N}_{O_3} = 0$, which corresponds to the complete conversion of one or all the reactants in the fast irreversible reaction, in fact represents a combination of the two different pseudo-steady-state hypothesis approximations for the species O and O_3, as both $N_O = 0$ and $N_{O_3} = 0$ satisfy the constraint.

Remark 5. For the pseudo-steady-state hypothesis for the species O (that is, $N_O = 0$), the algebraic variable in Eq. 38 reduces to $z = r_1$, and a reduced-order model with an overall stoichiometry of $2O_3 \rightarrow 3O_2$ (see Remark 3) is obtained as

$$\begin{bmatrix}\dot{N}_{O_2}\\ \dot{N}_{O_3}\\ \dot{T}\end{bmatrix} = \begin{bmatrix} 3\\ -2\\ \dfrac{2H_{O_3} - 3H_{O_2}}{NC_p}\end{bmatrix} r_1 V. \tag{40}$$

For the pseudo-steady-state hypothesis for the species O_3 (that is, $N_{O_3} = 0$), the algebraic variable in Eq. 38 reduces to $z = r_2$, and a reduced-order model with an overall stoichiometry of $2O \rightarrow O_2$ (see Remark 3) is obtained as

$$\begin{bmatrix}\dot{N}_O\\ \dot{N}_{O_2}\\ \dot{T}\end{bmatrix} = \begin{bmatrix} -2\\ 1\\ \dfrac{2H_O - H_{O_2}}{NC_p}\end{bmatrix}(r_2 + r_5)V. \tag{41}$$

Figures 4 and 5 show the composition and temperature profiles obtained from the reduced-order model in Eq. 39 and the full-order model in Eq. 36 for the initial condition $x = [0.02 \quad 0.9 \quad 0.1 \quad 400]^T$. It can be observed that after an initial fast transient the two models are in excellent agreement.

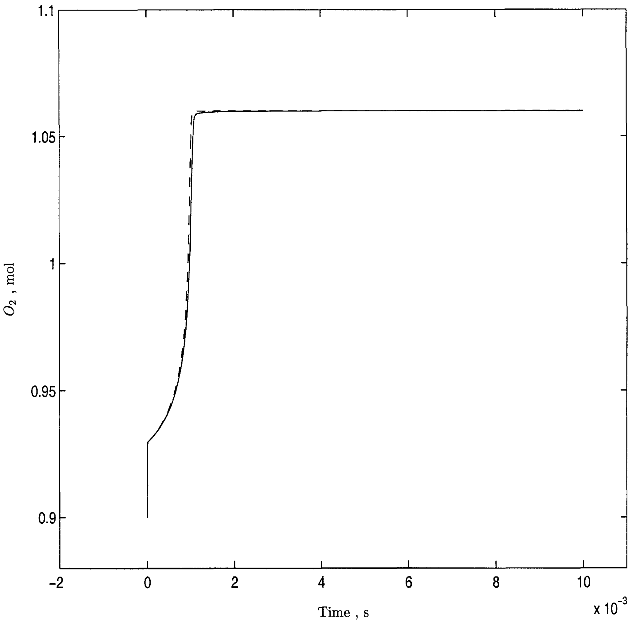

Figure 4. O_2 **profile for full-order system (solid) and reduced-order system (dash).**

Esterification of carboxylic acid

In this reaction system the esterification of a carboxylic acid (RCOOH) with an alcohol (R′OH) takes place in the presence of a homogeneous acid catalyst (HX) (Haario et al. 1999). The reaction proceeds through the acid-catalyzed formation of a carbenium ion ($RC^+(OH)_2$), which is subject to a nucleophilic attack from the alcohol. Furthermore, the acid catalyst can be esterified with the alcohol. For this reaction mechanism, the nucleophilic substitutions are considered rate determining (that is, these reactions are slow), and the subsequent rearrangement steps are fast reactions (for more discussion on the chemistry of the system, see Rönnback et al. (1997) and Streitwieser et al. (1992)). The overall system comprises 11 species and 12 elementary reactions occurring at constant temperature and pressure, which are summarized in Table 3. Although the exact kinetic data for all the reactions are not available, the relative order of magnitude of the reaction rate constants is known (Streitweiser, 1992). For notational simplicity, we assign a letter to each species instead of their respective molecular formula. Let $A = R'OH$, $B = RCOOH$, $C = RCOOR'$, $D = H_2O$, $E = H_3O^+$, $F = HX$, $G = RC^+(OH)_2$, $J = RCOO^-$, $K = R'OH_2^{\,+}$, $L = R'X$ and $X = X$. The full-order model comprises 11 differential equations, corresponding to each species composition, and its representation in the form of Eq. 3 is as follows

$$\begin{bmatrix} \dot{C}_A \\ \dot{C}_B \\ \dot{C}_C \\ \dot{C}_D \\ \dot{C}_E \\ \dot{C}_F \\ \dot{C}_G \\ \dot{C}_J \\ \dot{C}_K \\ \dot{C}_L \\ \dot{C}_X \end{bmatrix} = \begin{bmatrix} 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & -1 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ -1 & 1 & 0 & -1 & 1 & 1 & 1 & -1 & 0 & 1 & -1 & -1 \\ 1 & -1 & 1 & 1 & -1 & 0 & -1 & 1 & -1 & -1 & 1 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & -1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \\ r_5 \\ r_6 \\ r_7 \\ r_8 \\ r_9 \\ r_{10} \\ r_{11} \\ r_{12} \end{bmatrix}. \quad (42)$$

Reactions 3, 6, 9 and 12 are the slow reactions, and the remaining reactions are the fast reactions. Assuming that the reaction rate constants for all the fast reactions are of the same order of magnitude, we can define a hypothetical large parameter k^* such that $k_i/k^* \ll O(1)$ for $i = 3, 6, 9, 12$. This results in a partition of Eq. 42 similar to Eq. 5, and defining a small-parameter $\epsilon = 1/k^*$, the system of Eq. 42 can be writ-

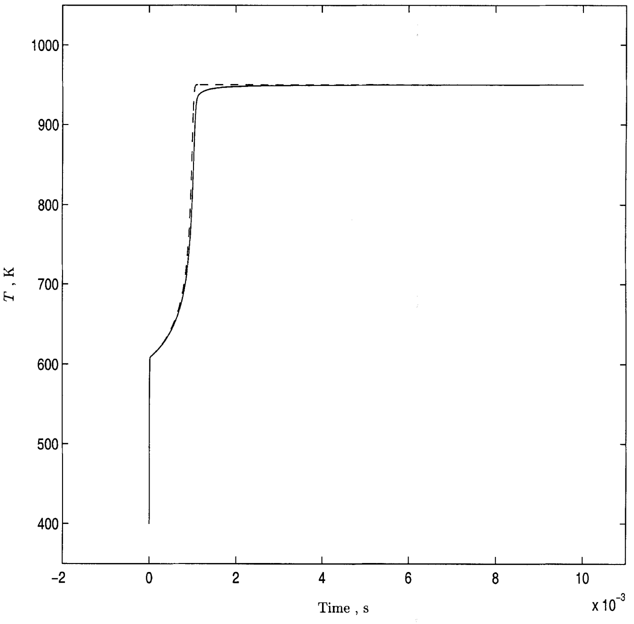

Figure 5. T **profile for full-order system (solid) and reduced-order system (dash).**

Table 3. Reaction Mechanism of Esterification of Carboxylic Acid

No. (R_i)	Reaction	Relative Speed
1	$HX+H_2O \rightarrow H_3O^+ + X$	Fast
2	$H_3O^+ + RCOOH \rightarrow RC^+(OH)_2 + H_2O$	Fast
3	$R'OH + RC^+(OH)_2 \rightarrow H_3O^+ + RCOOR'$	Slow
4	$RCOOH + H_2O \rightarrow RCOO^- + H_3O^+$	Fast
5	$R'OH + H_3O^+ \rightarrow H_2O + R'OH_2{}^+$	Fast
6	$X + R'OH_2{}^+ \rightarrow R'X + H_2O$	Slow
7	$H_3O^+ + X \rightarrow HX + H_2O$	Fast
8	$RC^+(OH)_2 + H_2O \rightarrow H_3O^+ + RCOOH$	Fast
9	$H_3O^+ + RCOOR' \rightarrow R'OH + RC^+(OH)_2$	Slow
10	$RCOO^- + H_3O^+ \rightarrow RCOOH + H_2O$	Fast
11	$H_2O + R'OH_2{}^+ \rightarrow R'OH + H_3O^+$	Fast
12	$R'X + H_2O \rightarrow X + R'OH_2{}^+$	Slow

ten in the form of Eq. 10 as

$$\begin{bmatrix} \dot{C}_A \\ \dot{C}_B \\ \dot{C}_C \\ \dot{C}_D \\ \dot{C}_E \\ \dot{C}_F \\ \dot{C}_G \\ \dot{C}_J \\ \dot{C}_K \\ \dot{C}_L \\ \dot{C}_X \end{bmatrix} = \begin{bmatrix} -1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & -1 & 0 \\ 0 & 1 & 0 & -1 \\ 1 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \\ -1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 1 \\ 0 & 1 & 0 & -1 \\ 0 & -1 & 0 & 1 \end{bmatrix} \begin{bmatrix} \bar{r}_3 \\ \bar{r}_6 \\ \bar{r}_9 \\ \bar{r}_{12} \end{bmatrix}$$

$$+ \frac{1}{\epsilon} \begin{bmatrix} 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 \\ 0 & -1 & -1 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 1 & -1 & 1 & 1 & -1 & 1 & -1 \\ 1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 \\ -1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \bar{r}_1 \\ \bar{r}_2 \\ \bar{r}_4 \\ \bar{r}_5 \\ \bar{r}_7 \\ \bar{r}_8 \\ \bar{r}_{10} \\ \bar{r}_{11} \end{bmatrix}. \quad (43)$$

Observe that the generalized stoichiometric matrix for the fast reactions is rank deficient (rank $(\mathcal{V}_f) = 4$). We can easily construct a matrix $\mathcal{V}_f'$ with full column rank, by selecting the first four columns of $\mathcal{V}_f$. This allows us to obtain the transformed reaction rates $\bar{r}_f'(x)$ (see Eq. 15), and in the limit as $\epsilon \rightarrow 0$, we obtain the algebraic constraints $\bar{r}_f'(x) = 0$ as

$$0 = C_F C_D - \frac{C_E C_X}{\kappa_1}$$

$$0 = C_E C_B - \frac{C_G C_D}{\kappa_2}$$

$$0 = C_B C_D - \frac{C_J C_E}{\kappa_4}$$

$$0 = C_A C_E - \frac{C_D C_K}{\kappa_5}, \quad (44)$$

where κ_j denotes the reaction equilibrium constant for the fast reversible reactions ($j = 1, 2, 4, 5$), with $\kappa_1 = k_1/k_7$, $\kappa_2 = k_2/k_8$, $\kappa_3 = k_4/k_{10}$, and $\kappa_4 = k_5/k_{11}$. Observe that the constraints in Eq. 44 correspond to the thermodynamic condition of chemical reaction equilibrium for the fast reversible reactions. Note that these algebraic constraints would have been obtained in a straightforward fashion, if to begin with the reactions were treated as reversible.

Note that the system is isothermal, and as such the distribution spanned by the columns of the stoichiometric matrix is involutive, and hence the true slow variables are readily obtained by evaluating Φ in $\zeta = \Phi x$, where Φ belongs to the null space of $\mathcal{V}_f'^T$. The resulting coordinate change is

$$\begin{bmatrix} \zeta_1 \\ \zeta_2 \\ \zeta_3 \\ \zeta_4 \\ \zeta_5 \\ \zeta_6 \\ \zeta_7 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 1 & 0 & 1 & 0 & -1 & 0 & 2 & 0 & 0 & 0 \\ -1 & 1 & 0 & -1 & 0 & 1 & 2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\times \begin{bmatrix} C_A \\ C_B \\ C_C \\ C_D \\ C_E \\ C_F \\ C_G \\ C_J \\ C_K \\ C_L \\ C_X \end{bmatrix}. \quad (45)$$

It should be noted that the slow variables obtained using the asymptotic expansion approach in Haario et al. (1999) for this system also belong to the null space of $\mathcal{V}_f'^T$; however the derivation in Haario et al., (1999) is considerably more tedious. The state-space realization of the reduced-order model in the new coordinates can be obtained as

$$\begin{bmatrix} \dot{\zeta}_1 \\ \dot{\zeta}_2 \\ \dot{\zeta}_3 \\ \dot{\zeta}_4 \\ \zeta_5 \\ \dot{\zeta}_6 \\ \dot{\zeta}_7 \end{bmatrix} = \begin{bmatrix} 0 & -1 \\ 0 & 1 \\ -1 & -1 \\ -1 & 1 \\ -1 & -1 \\ 1 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} \gamma_3(\zeta) \\ \gamma_6(\zeta) \end{bmatrix}, \quad (46)$$

where γ_3 and γ_6 represent the reaction rates of the slow reactions in the transformed coordinates. Note that the reduced-order model of the slow dynamics requires only the reaction equilibrium constants for the fast reversible reactions (to enforce the constraints), which can be determined with relatively more certainty than the reaction rate constants of the fast irreversible reactions.

Conclusions

In the present work, we presented a nonlinear model-reduction method for a broad class of nonisothermal reaction systems that exhibit dynamics in two different time scales, owing to the presence of fast and slow reactions. Specifically, we outlined a formulation of the standard material and energy balance model of such reaction systems that leads to a system of ODEs containing a small, singular perturbation parameter (the inverse of a "large" reaction rate constant). We derived a description of the slow dynamics of this system (in the limit as the singular perturbation parameter tends to 0) and showed this description to be a differential algebraic equation (DAE) system of high index. It was shown that the "singular" algebraic equations that are naturally obtained in this description correspond to reaction equilibrium or complete conversion constraints, for fast reversible and irreversible reactions, respectively. Then the derivation of reduced-order ODE models (DAE systems of index one) in terms of original state variables was described, and insight into the construction of nonlinear coordinate changes that allow deriving reduced-order state-space realizations of this DAE system was provided. We illustrated the developed modeling and reduction framework throughout with the classic Michaelis-Menten reaction system. Finally, the proposed model-reduction method was applied to two realistic reaction systems, while highlighting in particular how classic assumptions such as reaction equilibrium for fast reactions arise naturally from the proposed framework. Specifically, we studied an ozone decomposition reaction system, and demonstrated how the proposed framework encompasses various reduced models obtained by classic approximations valid under different initial and/or operating conditions. Following this, we studied the reaction kinetics for the esterification of carboxylic acid, and demonstrated the applicability of the proposed method to cases where the kinetic data for all reactions in the detailed reaction mechanism are not known. A future communication will address the extension of the developed method to reaction systems with dynamics in more than two time scales.

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Literature Cited

Aris, R., *Elementary Chemical Reactor Analysis*, Reprints Series in Chemical Engineering, Butterworths, London (1989).

Aris, R., and G. R. Gavalas, "On the Theory of Reactions in Continuous Mixtures," *Philos. Trans. R. Soc.*, **A260**, 351 (1966).

Astarita, G., and R. Ocone, "Chemical Reaction Engineering of Complex Mixtures," *Chem. Eng. Sci.*, **47**, 2135 (1992).

Bailey, G. E., and D. F. Ollis, *Biochemical Engineering Fundamentals*, Chemical Engineering Series, McGraw-Hill, New York (1977).

Bailey, J. E., "Lumping Analysis of Reactions in Continuous Mixtures," *Chem. Eng. J.*, **3**, 52 (1972).

Bowen, J. R., A. Acrivos, and A. K. Oppenheim, "Singular Perturbation Refinement to Quasi-Steady State Approximation in Chemical Kinetics," *Chem. Eng. Sci.*, **18**, 177 (1963).

Breusegem, V. V., and G. Bastin, "Reduced Order Dynamical Modelling of Reaction Systems: A Singular Perturbation Approach," *Proc. Conf. on Decision and Control*, Brighton, England, p. 1049 (1991).

Fraser, S. J., "The Steady State and Equilibrium Approximations: A Geometric Picture," *J. Chem. Phys.*, **88**, 4732 (1988).

Haario, H., L. Kalachev, T. Salmi, and J. Lehtonen, "Asymptotic Analysis of Chemical Reactions," *Chem. Eng. Sci.* **54**, 1131 (1999).

Kee, R. J., F. M. Rupley, and J. A. Miller, *Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics*, Sandia Rep. SAND89-8009B, UC-706, Sandia National Laboratories, Livermore, CA (1989).

Kumar, A., P. D. Christofides, and P. Daoutidis, "Singular Perturbation Modeling of Nonlinear Processes with Non-Explicit Time-Scale Separation," *Chem. Eng. Sci.*, **53**, 1491 (1998).

Kumar, A., and P. Daoutidis, *Control of Nonlinear Differential Algebraic Equation Systems*, Research Notes in Mathematics, Chapman & Hall/CRC, London (1999).

Lam, S. H., and D. A. Goussis, "The CSP Method for Simplifying Kinetics," *Int. J. Chem. Kinet.*, **26**, 461 (1994).

Li, G., and H. Rabitz, "A General Analysis of Exact Lumping in Chemical Kinetics," *Chem. Eng. Sci.* **44**, 1413 (1989).

Li, G., A. S. Tomlin, H. Rabitz, and J. Tóth, "A General Analysis of Approximate Nonlinear Lumping in Chemical Kinetics. I. Unconstrained Lumping," *J. Chem. Phys.*, **101**, 1172 (1994).

Maas, U., and S. B. Pope, "Simplifying Chemical Kinetics: Intrinsic Low-Dimensional Manifolds in Composition Space," *Combust. Flame*, **88**, 239 (1992).

Okino, M. S., and M. L. Mavrovouniotis, "Simplification of Mathematical Models of Chemical Reaction Systems," *Chem. Rev.*, **98**, 391 (1998).

Peters, N., *Reducing Mechanisms, Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames*, Springer-Verlag, Berlin (1991).

Petzold, L., and W. Zhu, "Model Reduction for Chemical Kinetics: An Optimization Approach," *AIChE J.*, **45**, 869 (1999).

Rabitz, H., M. Kramer, and D. Dacol, "Sensitivity Analysis of Chemical Kinetics," *Annu. Rev. Phys. Chem.*, **34**, 419 (1983).

Rönnback, R., T. Salmi, A. Vuori, H. Haario, J. Lehtonen, A. Sundqvist, and E. Tirronen, "Development of a Kinetic Model for the Esterification of Acetic Acid with Methanol in the Presence of a Homogeneous Acid Catalyst," *Chem. Eng. Sci.*, **52**, 3369 (1999).

Siegneur, C., G. Stephanopoulos, and R. W. Carr, Jr., "Dynamic Sensitivity Analysis of Chemical Reaction Systems," *Chem. Eng. Sci.*, **37**, 845 (1982).

Streitwieser, A., C. H. Heatcock, and E. M. Kusower, *Introduction to Organic Chemistry*, 4th ed., Macmillan, New York (1992).

Tomlin, A. S., G. Li, H. Rabitz, and J. Tóth, "A General Analysis of Approximate Nonlinear Lumping in Chemical Kinetics. I. Constrained Lumping," *J. Chem. Phys.*, **101**, 1188 (1994).

Turányi, T., T. Berces, and S. Vajda, "Reaction Rate Analysis of Complex Kinetic Systems," *Int. J. Chem. Kinet.*, **21**, 83 (1989).

Vajda, S., P. Valko, T. Turányi "Principal Component Analysis of Kinetic Models," *Int. J. Chem. Kinet.*, **17**, 55 (1985).

Vlachos, D. G., "Reduction of Detailed Kinetic Mechanisms for Ignition and Extinction of Premixed Hydrogen/Air Flames," *Chem. Eng. Sci.*, **51**, 3979 (1996).

Vora, N., *Nonlinear Model Reduction and Control of Multiple Time Scale Chemical Processes: Complex Reaction Systems and Reactive Distillation Columns*, Ph.D. Thesis, Univ. of Minnesota, Minneapolis (2000).

Wei, J., and J. C. W. Kuo, "A Lumping Analysis in Monomolecular Reaction Systems; Analysis of the Exactly Lumpable System," *Ind. Eng. Chem. Fundam.*, **8**, 114 (1969).

Williams, F. A., *Combustion Theory, The Fundamental Theory of Chemically Reactive Systems*, Benjamin/Cummings, Menlo Park, CA (1985).

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