Systematic approach for modeling reaction networks involving equilibrium and kinetically-limited reaction steps

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A B S T R A C T

Chemical systems often exhibit dynamics in different time scales owing to fast and slow reactions. Thus deriving models suitable for computation with standard numerical methods is challenging. In this tutorial we present a systematic approach for modeling chemical reaction systems including (known) slow reactions and fast reactions that can be assumed at equilibrium. The presented approach consists of the following steps: (i) identifying an independent set of reactions; (ii) writing the overall mass balance; (iii) writing a species balance for each species; (iv) writing the species transformation rates as a function of the net reaction rates; (v) introducing a constitutive equation for each reaction (either kinetic rate or equilibrium condition); (vi) performing index reduction of the differential-algebraic-equation (DAE) system. The resulting reduced system can be readily solved with standard DAE integrators. We discuss the number of initial conditions to be specified and illustrate the method through simple examples: methane reforming, Michaelis–Menten reaction and hydrogen-deuterium exchange.

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1. Introduction

Understanding chemical reaction kinetics is an important aspect in academic research and chemical industries. Reaction kinetics are used in various fields in chemistry and chemical engineering, e.g., mechanistic studies, catalyst development, process control and design, and process development (Berger et al., 2001). Understanding of reaction kinetics often comes from combining experimental studies and theoretical hypotheses, i.e., kinetic models. For model validation additional experiments have to be carried out.

Modeling reaction systems consists of defining a set of equations that describes the behavior of the system whether it be dynamic or stationary. However, finding a suitable set of equations can be challenging, e.g., when modeling dynamic systems involving multiple reaction steps. The equation system has to correctly describe the behavior of the reaction system and be well-posed. In addition some reactions may be kinetically-controlled whereas others may be so fast that they are always at equilibrium, which can result in problems in the correct definition of the variables and equations, and in numerical issues. An intrinsic part of modeling reaction network systems is identifying a constitutive equation for the reaction rates, which is quite challenging for fast kinetic rates. Moreover, resolving the fast kinetics numerically results in additional challenges (very stiff systems).

Many approaches exist in literature on how to derive the reaction rate equations, e.g., Rodin (1989), Carberry (1976), Carr (2007), Marin and Yablonsky (2011), Turanyi and Tomlin (2014), and Blackmond (2005). The reaction may be elementary, the rate is then proportional to the product of the substrates, or may follow a multi-step mechanism. In the latter case the reaction network

methods aim at model reduction and relaxation of the system's stiffness and can be divided into three general groups: reduction of number of species, e.g., elimination and lumping methods (Li and Rabitz, 1989; Li et al., 1994; Tomlin et al., 1994), reduction of number of reactions, e.g., elimination and sensitivity analysis methods (Turanyi et al., 1988; Turanyi, 1990), or decomposition of the motion dynamics into fast and slow, e.g., quasi-steady state and equilibrium assumption, slow or invariant manifold, singular perturbation and computational singular perturbation methods (Bowen et al., 1963; Heineken et al., 1967; Fraser, 1988; Maas and Pope, 1992; Rein, 1992; Lam and Goussis, 1994; Kumar et al., 1998; Vora and Daoutidis, 2001; Gorban and Karlin, 2003; Roussel and Zhu, 2004; Goussis and Valorani, 2006; Lee and Othmer, 2010; Goussis, 2012; Gupta et al., 2016).

The modeling of complex reaction networks where chemical species participate simultaneously in the fast (equilibrium) and slow (kinetically-controlled) reaction rates has been extensively studied in the past several decades. However, understanding and implementing these methods often requires considerable knowledge in the field. Complementing existing literature we present a simple tutorial that can be applied without extensive mathematical and/or modeling background. Herein, we focus on how to model dynamic reaction networks which exhibit different time dynamics, i.e., with equilibrium and kinetic reaction rates. We assume that the fast reactions are equilibrium reactions and that they are known. All non-equilibrium reactions are, therefore, considered to be slow kinetically-controlled reactions. As with all methodologies, this categorization of reactions has its limitations to all chemical systems (Turanyi et al., 1993; Goussis, 2012, 2015; Nicolas et al., 2015).

In this tutorial we describe step-by-step a systematic procedure on how to obtain a consistent set of model equations and initial conditions that is consistent with a general modeling framework for integral balance equations in a control volume (Bird, 1957; Bird et al., 1960), and specialize it to reactive systems. We first identify a consistent set of independent reactions and then write integral balance equations for the chemical species of the consistent set. In comparison to the slow reaction rates, the rates of the fast reactions are not a priori known, but rather derived using index reduction. Furthermore, the procedure can be easily incorporated into well known basic process modeling frameworks. Herein only lumped systems will be considered.

In the following sections we will present in detail on how the systematic approach can be applied to reaction networks with reaction rates in different time scales and illustrate the method via three simple examples.

2. A systematic approach to dynamic modeling

Consider a general multiple reaction system of the following form:

$$\sum_i A_i \overset{r_1}{\rightleftharpoons} \sum_i C_i$$
$$\vdots \qquad\qquad\qquad\qquad (1)$$
$$\sum_i A_i \overset{r_n}{\rightleftharpoons} \sum_i C_i$$

where A_i and C_i are all the possible chemical species that are consumed or produced, respectively, during a reaction step j, with $i = 1, \ldots, N_s$ and $j = 1, \ldots, N_r$, where N_s and N_r are the total number of species and reaction steps, respectively. The reversible reaction step j has a net reaction rate r_j and is composed of a forward and a backward reaction step:

$$r_j = r_{j,f} - r_{j,r} \qquad\qquad (2)$$

can be modeled via an overall rate equation or each reaction step can be modeled individually. Modeling the overall reaction rate can be done by eliminating the individual steps of the mechanism using different assumptions, such as quasi-steady state assumption (Carberry, 1976; Segel and Slemrod, 1989; Carr, 2007; Lazman and Yablonsky, 2008), equilibrium or partial equilibrium assumption (Turanyi and Tomlin, 2014). Generally, for large reaction networks, the overall rate equation is complicated, incorporating terms for all the reaction rates and their corresponding rate parameters. However, not all steps have the same influence on the dynamics of the various system species. Therefore, the overall rate can often be simplified (Turanyi and Tomlin, 2014; Gorban et al., 2010; Marin and Yablonsky, 2011), e.g., assuming irreversibility of reaction steps and rate limiting steps, where only the corresponding limiting rate parameters are considered for the overall rate equation and the others are neglected.

The derivation of the overall rate is not always necessary and each single step of the reaction network can be modeled individually. In this case a reaction rate has to be defined for each single step. Often the reaction rate follows elementary reaction kinetics. When modeling complex reaction networks it is often difficult to incorporate reaction rates with different dynamics into the system model. Such networks often result in large, stiff dynamic systems. Multiple valid approaches on how to model such systems exist (Susnow et al., 1997; Okino and Mavrovouniotis, 1998; Haseltine and Rawlings, 2002; Nicolas et al., 2015; Daoutidis, 2015). These