CONCEPT AND APPLICATIONS OF EXTENTS IN CHEMICAL REACTION SYSTEMS

D. Bonvin*, S. Srinivasan, D. Rodrigues, J. Billeter and M. Amrhein

Laboratoire d'Automatique, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

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Abstract

Models of chemical reaction systems can be quite complex as they need to include information regarding the reactions and the transfer of mass and heat. The commonly used state variables—concentrations and temperatures—describe the interplay between many phenomena. As a consequence, each state variable is affected by several rate processes. On the other hand, it is well known that it is possible to partition the state space into a reaction invariant subspace and its orthogonal complement using a linear transformation involving the reaction stoichiometry. This paper uses a more sophisticated linear transformation to partition the state space into various subspaces, each one linked to a single rate process such as a particular reaction, a mass or heat transfer, an inlet or outlet flow. The implications of this partitioning are discussed with respect to several applications dealing with modeling, estimation, control and optimization.

Keywords

Chemical reaction systems, Reaction variants, Vessel extents, State transformation, Model reduction, Shape constraints.

Introduction

The chemical industry uses reaction processes to convert raw materials into desired products. The models of chemical reaction processes are typically first-principles models that describe the evolution of the total mass, the concentrations and the temperature by means of balance equations of differential nature (continuity equation, molar balances, heat balances) and constitutive equations of algebraic nature (equilibrium relationships, rate expressions). A reliable description of reaction kinetics and transport phenomena represents the main challenge in building first-principles models for chemical reaction systems.

The presence of all these phenomena, and in particular their interactions, complicates the analysis and operation of chemical reactors. The analysis would be much simpler if one could somehow separate the effect of the various phenomena and investigate each phenomenon individually. Ideally, one would like to have decoupled states, where each state depends on a single rate process. Note that some of the state variables are often redundant, as there are typically more states (balance equations) than there are independent sources of variability (reactions, exchange terms).

Asbjørnsen and Fjeld (1970) introduced the concepts of *reaction variants and invariants* and used them for reactor modeling and control. However, these reaction variants encompass more than the reaction contributions since they are also affected by the inlet and outlet flows. Amrhein et al. (2010) showed that, for a homogeneous reactor with outlet, the concept of *vessel extent* is most useful, as it represents the amount of material associated with a given rate process (reaction, exchange) that is still in the vessel. Bhatt et al. (2010) extended that concept to multiphase reaction systems.

Various applications of the concept of reaction variants/invariants have been studied in the literature. For example, Srinivasan et al. (1998) discussed the implications of reaction and flow variants/invariants for control-

*To whom all correspondence should be addressed
dominique.bonvin@epfl.ch

related tasks such as model reduction, state accessibility, state reconstruction and feedback linearizability. Furthermore, control laws using reaction variants have been proposed for continuous stirred-tank reactors (Hammarstrom, 1979; Waller and Mäkilä, 1981; Zhao et al., 2016).

This paper addresses the analysis of chemical reaction systems and the possibility of isolating the effects of the various rate processes. Two transformations of the mole balance equations will be presented. It will be shown that, not only can reaction-variant states be separated from reaction-invariant states, but a much finer partitioning can be achieved via the concept of vessel extents. The objective of this paper is therefore to sketch new avenues that could possibly lead to improved estimation, control and optimization of reaction systems.

The paper is organized as follows. After a review of two state transformations for open homogeneous reactors, we present ways of computing the vessel extents from concentration and spectral measurements. Then, the implications of being able to separate the effects of the various rate processes are discussed in connection with several applications.

Alternative State Representations

This section presents alternative state representations for open homogeneous reaction systems. The basic model consists of the mole balance equations. The alternative representations are obtained via state transformation of the basic model. One representation is based on reaction-variant and reaction-invariant states, while the second representation relies on vessel extents. Extensions to heterogeneous reaction systems, to systems including a heat balance equation, and to distributed reaction systems can be found in Rodrigues et al. (2015b).

1. Mole Balance Equations (S species)

The mole balances for an open non-isothermal homogeneous reaction system involving S species, R reactions, p inlet streams and one outlet stream can be written as follows:

$$\dot{\mathbf{n}}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}\,\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}(t), \quad \mathbf{n}(0) = \mathbf{n}_0, \quad (1)$$

with $\mathbf{r}_v(t) := V(t)\,\mathbf{r}(t)$ and $\omega(t) := \frac{u_{out}(t)}{m(t)}$ the inverse of the residence time, and where $\mathbf{n}(t)$ is the S-dimensional vector of numbers of moles, $\mathbf{r}(t)$ the R-dimensional reaction rate vector, $\mathbf{u}_{in}(t)$ the p-dimensional inlet mass flowrate vector, $u_{out}(t)$ the outlet mass flowrate, $V(t)$ and $m(t)$ the volume and the mass of the reaction mixture. $\mathbf{N}$ is the $R\times S$ stoichiometric matrix, $\mathbf{W}_{in}$ the $S\times p$ inlet-composition matrix, and $\mathbf{n}_0$ the S-dimensional vector of initial numbers of moles.

Model (1) holds independently of the concentration and temperature conditions since the reaction rates are simply modeled as the unknown time signals $\mathbf{r}(t)$, that is, as *endogenous inputs*. However, the concentrations $\mathbf{c}(t)$ and the temperature $T(t)$ affect the reaction rates through the relations $\mathbf{r}(t) = \boldsymbol{\phi}_r\big(\mathbf{n}(t), T(t)\big)$. If needed, one can compute the volume as $V(t) = \phi_V\big(\mathbf{n}(t), T(t)\big)$ and the concentrations as $\mathbf{c}(t) = \mathbf{n}(t)/V(t)$.

The mass flowrates $\mathbf{u}_{in}(t)$ and $u_{out}(t)$ are typically considered as exogenous inputs in Eq. (1). The continuity equation (or total mass balance) is given by:

$$\dot{m}(t) = \mathbf{1}_p^{\mathrm{T}}\mathbf{u}_{in}(t) - u_{out}(t), \qquad m(0) = m_0, \quad (2)$$

where $\mathbf{1}_p$ is the p-dimensional vector filled with ones and m_0 the initial mass. Note that the mass $m(t)$ can also be computed from the numbers of moles $\mathbf{n}(t)$ as $m(t) = \mathbf{1}_S^{\mathrm{T}}\,\mathbf{M}_w\,\mathbf{n}(t)$, which indicates that Eq. (1) and Eq. (2) are in fact linearly dependent. The volume $V(t)$ can be inferred from the mass and knowledge of the density ρ as $V(t) = m(t)/\rho(t)$. Note that $\rho(t)$ can be expressed as $\rho(t) = \phi_\rho\big(\mathbf{n}(t), T(t)\big)$.

If the stoichiometric matrix is unknown, it can be inferred from measurements using target factor analysis (TFA) (Amrhein et al., 1999). TFA has been used successfully to determine the number of independent reactions R and the corresponding stoichiometric matrix $\mathbf{N}$ using concentration and flowrate measurements.

2. Reaction Variants and Invariants (S abstract states)

Asbjørnsen and Fjeld (1970) used the stoichiometric matrix $\mathbf{N}$ to construct a linear transformation of the states $\mathbf{n}(t)$ to the reaction-variant states $\mathbf{y}_{rv}(t)$ and the reaction-invariant states $\mathbf{y}_{ri}(t)$. This transformation $\mathcal{T} : \mathbb{R}^S \to \mathbb{R}^S$ involves the matrix $\mathbf{N}$ and its null space of dimension $(S-R)$ described by the $S\times(S-R)$ matrix $\mathbf{P}$, that is, $\mathbf{N}\,\mathbf{P} = \mathbf{0}_{R\times(S-R)}$:

$$\begin{bmatrix}\mathbf{y}_{rv}(t)\\ \mathbf{y}_{ri}(t)\end{bmatrix} = \mathcal{T}\,\mathbf{n}(t) \quad \text{with} \quad \mathcal{T} := \begin{bmatrix}\mathbf{N}^{\mathrm{T}} & \mathbf{P}\end{bmatrix}^{-1}. \quad (3)$$

The resulting dynamical system contains the R state variables $\mathbf{y}_{rv}(t)$ that depend on the reactions and the $(S-R)$ state variables $\mathbf{y}_{ri}(t)$ that do not:

$$\begin{aligned}\dot{\mathbf{y}}_{rv}(t) &= \mathbf{r}_v(t) + (\mathbf{N}^{\mathrm{T}})^{+}\,\mathbf{W}_{in}\,\mathbf{u}_{in}(t) - \omega(t)\,\mathbf{y}_{rv}(t)\\ &\qquad\qquad \mathbf{y}_{rv}(0) = (\mathbf{N}^{\mathrm{T}})^{+}\,\mathbf{n}_0\\ \dot{\mathbf{y}}_{ri}(t) &= \mathbf{P}^{+}\,\mathbf{W}_{in}\,\mathbf{u}_{in}(t) - \omega(t)\,\mathbf{y}_{ri}(t)\\ &\qquad\qquad \mathbf{y}_{ri}(0) = \mathbf{P}^{+}\,\mathbf{n}_0,\end{aligned} \quad (4)$$

where $(\mathbf{N}^{\mathrm{T}})^{+}$ is the Moore-Penrose pseudo-inverse of $\mathbf{N}^{\mathrm{T}}$. The numbers of moles $\mathbf{n}(t)$ can be reconstructed from the reaction variants and invariants as:

$$\mathbf{n}(t) = \mathcal{T}^{-1} \begin{bmatrix} \mathbf{y}_{rv}(t) \\ \mathbf{y}_{ri}(t) \end{bmatrix} = \mathbf{N}^{\mathrm{T}}\, \mathbf{y}_{rv}(t) + \mathbf{P}\, \mathbf{y}_{ri}(t). \tag{5}$$

Remarks. The reaction variants are decoupled with respect to the reaction rates, that is, $y_{rv,i}(t)$ depends on $r_{v,i}(t)$ but not on the other reaction rates. However,

- $\mathbf{y}_{rv}$ are reaction *and* flow variants,
- $\mathbf{y}_{ri}$ are reaction invariants but flow variants, hence not true invariants,
- $\mathbf{y}_{rv}$ are pure reaction variants and $\mathbf{y}_{ri}$ are true invariants only for batch reactors.

Hence, the question arises whether it is possible to compute pure reaction variants and true invariants for open reactors, thereby removing the effect of the inlet and outlet flows. The next section will show that this is possible with the concept of vessel extents.

3. Vessel Extents (d extents)

The concept of vessel extents was introduced by Amrhein et al. (2010) and reformulated by Rodrigues et al. (2015b). Only the key equations will be given next.

Consider the $S \times d$ matrix $\mathbf{B} := \begin{bmatrix} \mathbf{N}^{\mathrm{T}} & \mathbf{W}_{in} & \mathbf{n}_0 \end{bmatrix}$ of rank d, where $d := R + p + 1$ is the number of independent *exogenous and endogenous* inputs. The transformation $\mathcal{T} : \mathbb{R}^S \to \mathbb{R}^S$ involves the matrix $\mathbf{B}$ and its left null space of dimension $q := S - d$ described by the $S \times q$ matrix $\mathbf{P}$, that is, $\mathbf{B}^{\mathrm{T}}\, \mathbf{P} = \mathbf{0}_{d \times q}$:

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \\ \mathbf{x}_{iv}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{R} \\ \mathbf{F} \\ \mathbf{i}^{\mathrm{T}} \\ \mathbf{P}^{+} \end{bmatrix} \mathbf{n}(t) = \mathcal{T}\, \mathbf{n}(t) \quad \text{with} \quad \mathcal{T} := \begin{bmatrix} \mathbf{B} & \mathbf{P} \end{bmatrix}^{-1}. \tag{6}$$

The transformed model is in the decoupled form:

$$\dot{x}_{r,i}(t) = r_{v,i}(t) - \omega(t)\, x_{r,i}(t), \qquad x_{r,i}(0) = 0, \quad i = 1, \ldots, R \tag{7a}$$

$$\dot{x}_{in,j}(t) = u_{in,j}(t) - \omega(t)\, x_{in,j}(t), \qquad x_{in,j}(0) = 0, \quad j = 1, \ldots, p \tag{7b}$$

$$\dot{x}_{ic}(t) = -\omega(t)\, x_{ic}(t), \qquad x_{ic}(0) = 1 \tag{7c}$$

$$\mathbf{x}_{iv}(t) = \mathbf{0}_q\,, \tag{7d}$$

where $x_{r,i}(t)$ is the extent of the i^{th} reaction at time t expressed in kmol, $x_{in,j}(t)$ the extent of the j^{th} inlet flow at time t expressed in kg, $x_{ic}(t)$ the dimensionless extent of initial conditions that indicates the fraction of the initial conditions that is still in the reactor at time t, and $\mathbf{x}_{iv}(t)$ the vector of invariants at time t. Note that each extent is affected by its corresponding rate process (either $r_{v,i}(t)$, $u_{in,j}(t)$ or $\delta(t)$[1]) and, in the presence of an outlet, also by the inverse residence time $\omega(t)$. Since each extent is discounted by the amount of material that has left the reactor, it represents the amount of material associated with the corresponding rate that is still in the vessel. Hence, these extents are called "vessel extents". The numbers of moles $\mathbf{n}(t)$ can be reconstructed from the various extents as $\mathbf{n}(t) = \mathcal{T}^{-1}\, \mathbf{x}(t)$, that is,

$$\mathbf{n}(t) = \mathbf{N}^{\mathrm{T}} \mathbf{x}_r(t) + \mathbf{W}_{in} \mathbf{x}_{in}(t) + \mathbf{n}_0\, x_{ic}(t). \tag{8}$$

Properties

- *Dimensionality reduction.* The q invariants $\mathbf{x}_{iv}(t)$ are identically equal to zero and can be discarded from the model. Hence, the dynamic model is of order $R + p + 1 \leq S$. The extents $\mathbf{x}_{in}(t)$ and $x_{ic}(t)$ and the mass $m(t)$ can be computed from $\mathbf{u}_{in}(t)$ and $u_{out}(t)$ using Eqs (7b) and (7c) and the continuity equation (2). Note that $\mathbf{x}_{iv}(t) = \mathbf{0}_q$ generates the important invariant relationships $\mathbf{P}^{+}\, \mathbf{n}(t) = \mathbf{0}_q$.

- *Decoupling.* The extent of reaction $x_{r,i}(t)$ depends upon the corresponding reaction rate $r_{v,i}(t)$ and the inlet and outlet flows, but not on the other rate processes. It follows that $r_{v,i}(t)$ can be computed solely from $x_{r,i}(t)$, its time derivative and $\omega(t)$, that is, without having to know the other extents.[2]

- *Monotonicity, Convexity/Concavity.* Since each vessel extent is affected by a single rate function, these extents are more likely to exhibit monotonicity or convexity/concavity properties than the concentration profiles. These properties can be used to improve computational tasks such as data reconciliation and state estimation as discussed below. If needed, the shape can also be inferred from measurements. One approach computes the upper and lower bounds on the first and second derivatives of the extents obtained from measurements. It follows that an extent is monotonically increasing if the lower bound on its first derivative is positive. Similarly, an extent is concave if the upper bound on its second derivative is negative (Srinivasan, 2016).

[1] Eq. (7c) can be written as $\dot{x}_{ic}(t) = \delta(t) - \omega(t)\, x_{ic}(t),\ x_{ic}(0) = 0$.

[2] This apparent decoupling is somewhat misleading: indeed, since $r_{v,i}(t)$ is an endogenous signal, it depends on what happens in the reactor, that is, it also depends indirectly on the other extents via the concentrations.

Vessel Extents from Measurements

The vessel extents can be computed from the numbers of moles using Eq. (6). Note that it is not necessary to have S measured numbers of moles to compute all the vessel extents. Let us assume that there are S_a available (measured) species, with the subscript $(\cdot)_a$ denoting a quantity associated with the available species. One can compute the numbers of moles as follows:

1. From Measurements $\mathbf{n}_a$

If $S_a \geq d$, the transformation $\mathcal{T}_a : \mathbb{R}^{S_a} \rightarrow \mathbb{R}^d$ gives

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \end{bmatrix} = \mathcal{T}_a \, \mathbf{n}_a(t) \quad \text{with} \quad \mathcal{T}_a := \begin{bmatrix} \mathbf{B}_a & \mathbf{P}_a \end{bmatrix}^{-1}, \tag{9}$$

which requires $rank(\mathbf{B}_a) = d$. One also has the $q_a := S_a - d$ invariant relationships $\mathbf{P}_a^+ \, \mathbf{n}_a(t) = \mathbf{0}_{q_a}$.

2. From Measurements $\mathbf{n}_a$, $\mathbf{u}_{in}$ *and* u_{out}

If the inlets $\mathbf{u}_{in}(t)$ and the inverse residence time $\omega(t)$ are known, one can compute $\mathbf{x}_{in}(t)$ and $x_{ic}(t)$ from numerical integration of Eqs (7b)-(7c). Then, Eq. (8) can be used to compute the reaction contributions in $\mathbf{n}_a(t)$, labeled the numbers of moles in *vessel reaction-variant (vRV) form*, as follows:

$$\mathbf{n}_a^{vRV}(t) := \mathbf{n}_a(t) - \mathbf{W}_{in,a}\mathbf{x}_{in}(t) - \mathbf{n}_{a,0}\, x_{ic}(t), \tag{10}$$

which allows writing $\mathbf{n}_a^{vRV}(t) = \mathbf{N}_a^{\mathrm{T}} \, \mathbf{x}_r(t)$ and

$$\mathbf{x}_r(t) = (\mathbf{N}_a^{\mathrm{T}})^+ \, \mathbf{n}_a^{vRV}(t). \tag{11}$$

Eq. (11) requires $rank(\mathbf{N}_a) = R$, and thus $S_a \geq R$.

3. From Spectroscopic Measurements

Since direct concentration measurements are typically not available during the reaction, online spectral measurements can be used to estimate concentrations delay-free at high sampling rates. Multivariate calibration models are typically used for concentration estimation. As an alternative, multivariate curve resolution (MCR) techniques allow determining $\mathbf{C}$ and $\mathbf{E}$ from the $K \times L$ spectral measurement matrix $\mathbf{A}$, assuming the bilinear model $\mathbf{A} = \mathbf{C}\,\mathbf{E}$, with $\mathbf{C}$ being the $K \times S$ concentration matrix and $\mathbf{E}$ the $S \times L$ pure-component spectral matrix.

An important MCR technique is alternative regression, which solves alternatively for $\mathbf{E}$ and $\mathbf{C}$, each time imposing constraints on the solution. It turns out that it is much simpler to work in a lower-dimensional space with the R extents of reaction as decision variables instead of the S-dimensional concentration vector. For this, the matrix $\mathbf{A}$ is simply factorized in vRV form. Details are found in Billeter et al. (2016).

Use of Vessel Extents to Improve Measurements

The concept of vessel extents is quite useful to process measurements in order to reconstruct missing values or improve existing ones, as discussed next.

1. Reconstruction of Unmeasured Numbers of Moles

It is possible to reconstruct $\mathbf{n}(t)$ from a limited number of measured numbers of moles $\mathbf{n}_a(t)$ *without the use of kinetic information*. A common situation is the case $S_a \geq d$, whereby the extents $\mathbf{x}_r(t)$, $\mathbf{x}_{in}(t)$ and $x_{ic}(t)$ can be computed (via the linear transformation (9)) and $\mathbf{n}(t)$ reconstructed using Eq. (8). The idea is similar to that of the asymptotic observer proposed by Bastin and Dochain (1990).

More interesting is the case $d > S_a \geq R$, whereby $\mathbf{n}_a(t)$ can be reconstructed via the computation of $\mathbf{x}_r(t)$ (using the linear transformation (11)) and of $\mathbf{x}_{in}(t)$ and $x_{ic}(t)$ (from numerical integration of Eqs (7b)-(7c)).

For the case $S_a < R$, it is no longer possible to compute all extents of reaction from $\mathbf{n}_a(t)$ without kinetic information.

2. Data Reconciliation

Concentration measurements are invariably corrupted by measurement noise. Data reconciliation techniques reduce the noise in the measurements and improve their accuracy by using redundancies derived from conservation equations. In the absence of kinetic models, the available redundancies correspond to the q_a invariant relationships $\mathbf{P}_a^+ \, \mathbf{n}_a(t) = \mathbf{0}_{q_a}$. These relationships are static in nature since they only use information at the time instant t. Constraints such as monotonicity, concavity or convexity can be added to the data reconciliation problem to provide *dynamic* information regarding past and future measurements. Shape constraints are more likely to hold for vessel extents than for numbers of moles (Srinivasan et al., 2015).

Selected Applications

The benefit of using vessel extents is discussed next with respect to several applications.

1. Model Reduction

It is clear from Eq. (8) and the transformed system (7a)-(7c) that only d differential equations need to be integrated to compute the trajectories $\mathbf{n}(t)$. The dimensionality of the system is therefore $d = R + p + 1$.[3] This dimensionality can be reduced further by eliminating fast modes using, for example, singular-perturbation theory. It turns out that it is much easier to implement singular perturbations using the transformed system (7a)-(7c) than the original system (1) since the *reactions* (and not the numbers of moles) exhibit fast or slow dynamics. Along the same line, the concept of vessel extents has been used very advantageously toward the identification of multiphase reaction systems with instantaneous equilibria, that is, when certain reactions are very fast (Srinivasan et al., 2016a).

2. Kinetic Identification

Bhatt et al. (2012) have shown that incremental kinetic identification performed using the concept of vessel extents is computationally simpler and more effective than the simultaneous identification in terms of numbers of moles. With the incremental approach, model identification can be performed for each reaction *individually* and independently of the other reactions. For the i^{th} reaction, the kinetic model is identified from a set of model candidates by comparing the reconciled extent $\hat{x}_{r,i}$ with the model prediction $x_{r,i}$. However, this is obtained at the price of not guaranteeing parameter estimates in the maximum-likelihood sense because certain concentrations appearing in the rate laws need to be estimated through interpolation of noisy measured values.

Recently, Srinivasan (2016) proposed a novel sequential approach that combines the advantages of the incremental and simultaneous approaches. The method progresses sequentially from a purely incremental to a purely simultaneous approach. The identification of the last rate process is of the purely simultaneous type since all rate parameters are estimated simultaneously using the model structures that have been determined previously and the model candidates for the last rate. This leads to a parameter estimation in the maximum-likelihood sense.

[3]Note that the dimensionality of a CSTR with constant density is $d = R + p$ as shown in Rodrigues et al. (2015b).

3. State Estimation

Once kinetic models are available, state estimation can be used to improve the quality of measured signals and reconstruct unmeasured quantities. The idea here is to use additional shape constraints in the estimation problem. Formulating the state estimation problem in terms of vessel extents allows imposing shape constraints that are otherwise not present in concentration profiles. This improves the accuracy of the estimated states compared to the estimation without shape constraints (Srinivasan et al., 2016b).

4. Online Control

The control performance of chemical reactors can be improved if one can estimate (and predict) the various reaction rates. This typically requires the use of kinetic models. When such models are not available, one can proceed as follows: (i) estimate the extents of reaction from the measured quantities $\mathbf{n}_a(t)$ and knowledge of $\mathbf{u}_{in}(t)$ and $\omega(t)$ using Eq. (11); (ii) estimate $\mathbf{r}_v(t)$ via numerical differentiation of $\mathbf{x}_r(t)$ using, for example, the first-order filter proposed by Savitzky and Golay (1964). The latter can be shown to provide minimal variance among all unbiased rate estimators. Rodrigues et al. (2015a) presented an application of rate estimation for the purpose of data-driven control of a CSTR using feedback linearization.

5. Static Real-time Optimization

The concept of vessel extents can also be used to speed up the estimation of plant steady state without the use of kinetic models. This fast estimation reduces significantly the time it takes to compute the cost and constraints that are needed to implement static real-time optimization. The key idea stems from Eqs (7b) and (7c) which, at steady state, give $\bar{\mathbf{x}}_{in} = \frac{\bar{\mathbf{u}}_{in}}{\bar{\omega}}$ and $\bar{x}_{ic} = 0$, where $\bar{(\cdot)}$ denotes a quantity at steady state.

If the numbers of moles $\mathbf{n}_a(t)$ of the measured species and the volume $V(t)$ are controlled by manipulating $\mathbf{u}_{in}(t)$ and $\omega(t)$, then, as soon as $\mathbf{n}_a(t)$ and $V(t)$ reach steady state, the manipulated variables converge to $\bar{\mathbf{u}}_{in}$ and $\bar{\omega}$, and one can compute $\bar{\mathbf{x}}_{in}$. The extents of reaction at steady state can be estimated *without kinetic models* as $\bar{\mathbf{x}}_r = (\mathbf{N}_a^{\mathrm{T}})^+ (\bar{\mathbf{n}}_a - \mathbf{W}_{in,a}\bar{\mathbf{x}}_{in})$. Finally, the steady state of the numbers of moles $\mathbf{n}_u$ of the unmeasured species can be estimated as $\bar{\mathbf{n}}_u = \mathbf{N}_u^{\mathrm{T}}\bar{\mathbf{x}}_r + \mathbf{W}_{in,u}\bar{\mathbf{x}}_{in}$, and this *before* $\mathbf{n}_u$ reaches steady state. Details can be found in Rodrigues et al. (2016).

Conclusions

This paper has addressed the computation of variant and invariant quantities for open homogeneous reaction systems. Isolation of the individual rate processes is implemented via partitioning of the balance equations using a linear transformation. In a sense, one can say that this work extends the concept of batch extents to reactors with inlet and outlet flows. Note that these results are fairly general and carry over to cases that include a heat balance around the reactor and to multiphase reactors, for which there will be additional rate processes for heat flow and mass transfers (Rodrigues et al., 2015b).

This paper has also addressed the potential of the concept of vessel extents for applications such as kinetic identification, state estimation, control and optimization. The benefit of working explicitly with vessel extents instead of numbers of moles is twofold: (i) dimensionality reduction from S to d, and even to R if one can discount the effects of the inlet and outlet flows; and (ii) decoupling of the various rate processes, which allows dealing with each rate individually. More work is needed to consolidate some of the novel ideas presented in this paper.

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