Reaction and Flow Variants/Invariants in Chemical Reaction Systems with Inlet and Outlet Streams

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The concept of reaction invariants is extended to include flow invariants of chemical-reaction systems with inlet and outlet streams. A transformation to normal form is introduced that allows the separation of (1) the evolution of the independent reactions, (2) the influence of inlet streams, and (3) the behavior of the reaction and flow invariants. In the light of this transformation to normal form, model reduction, state accessibility, state reconstruction, and feedback linearizability are analyzed.

Introduction

Models of chemical reaction systems include information regarding both the chemical reactions (stoichiometry and kinetics) and the operation mode of the reactor. For the analysis of such models, it is important to distinguish between the states that intrinsically vary with time and those that do not. A transformation has been proposed by Waller and Mäkilä (1981) to separate the reaction variant (same dimension as the number of reactions) from the reaction invariant states. For reaction systems with neither inlet nor outlet streams, the complete concentration vector can then be reconstructed by integrating only the reaction variants.

For considerations of safety and productivity, however, the reactors used in the production of specialty chemicals are often of the semibatch type (systems with inlets), or run continuously (systems with inlet and outlets). The aim here is to extend the concept of invariance to chemical-reaction systems with inlet and outlet streams. This requires the concept of invariants to include flow invariants. A transformation to normal form is proposed herein that performs a three-level decomposition of the states into (1) the evolution of the reactions, (2) the influence of inlet streams, and (3) the behavior of the reaction and flow invariants. No kinetic information (except for the assumption of independent kinetics) is necessary for the analysis.

The proposed transformation to normal form helps determine the minimal dimensionality of the model (i.e., the minimal number of differential equations) and analyze control-relevant properties such as state accessibility and feedback linearizability. The important results regarding state accessibility proposed by Bastin and Lévine (1993) can be readily derived from the transformation to normal form. Under certain conditions, the system can be proven to be feedback linearizable, and the linearizing control can be obtained easily.

For simplicity, reaction systems with constant temperature, density, and inlet molar concentrations are considered first. However, isothermal operation is sometimes difficult to achieve or simply undesirable because it is nonoptimal. Furthermore, as a considerable effort is required to reduce the amount of solvent used in liquid-phase homogeneous reaction systems, the assumption of constant density is often not valid. Also, the inlet molar concentrations might vary due to variability in the raw materials or in the processing steps. Thus, the assumptions of constant temperature density and inlet molar concentration are relaxed, and indications for constructing the transformation to normal form are provided. Semibatch reaction systems and continuous stirred-tank reaction systems (CSTRs) are considered as special cases.

The next sections describe the basic model used in this study and develops the transformation to normal form and discusses some implications. Extensions to the basic model are discussed, as well as special cases and a simulated example are considered.

Model of a Homogeneous, Constant-Density, Isothermal Reaction System

Consider a homogeneous, constant-density, isothermal, semibatch or continuous stirred-tank chemical reaction system comprising S species and R independent reactions, *independent reactions* being those that have both independent stoichiometries *and* independent kinetics (Amrhein et al.,

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1996). The material balance equations and the continuity equation are described by:

$$\dot{\boldsymbol{n}} = V\boldsymbol{K}\boldsymbol{r}_n(\boldsymbol{n},V) + \boldsymbol{C}_{\text{in}}\boldsymbol{q}_{\text{in}} - (q_{\text{out}}/V)\boldsymbol{n}, \qquad \boldsymbol{n}(0) = \boldsymbol{n}_0,$$
$$\dot{V} = \left(\boldsymbol{1}_p^T\boldsymbol{q}_{\text{in}}\right) - q_{\text{out}}, \qquad V(0) = V_0, \quad (1)$$

where $\boldsymbol{n}$ is the S-dimensional vector of the number of moles; $\boldsymbol{q}_{\text{in}}$ the p-dimensional inlet volumetric flow-rate vector; q_{out} the outlet volumetric flow rate expressed as the sum of q outlet volumetric flow rates; V the reactor volume; $\boldsymbol{K}$ the $S \times R$ stoichiometric matrix; $\boldsymbol{r}_n$ the R-dimensional reaction-rate vector, which is a function of $\boldsymbol{n}$ and V; $\boldsymbol{C}_{\text{in}} = [\boldsymbol{c}_{\text{in}}^1, \ldots, \boldsymbol{c}_{\text{in}}^p]$; $\boldsymbol{c}_{\text{in}}^i$ the molar concentrations of the ith inlet stream; $\boldsymbol{n}_0$ the initial number of moles; V_0 the initial volume; and $\boldsymbol{1}_p$ a p-dimensional vector with all elements being 1. To completely describe Eq. 1, the R-dimensional vector function $\boldsymbol{r}_n(\boldsymbol{n},V)$ must be specified.

The terms $V\boldsymbol{K}\boldsymbol{r}_n(\boldsymbol{n},V)$, $\boldsymbol{C}_{\text{in}}\boldsymbol{q}_{\text{in}}$, and $(q_{\text{out}}/V)\boldsymbol{n}$ represent the effect of the reactions, the inlet streams, and outlet stream on the number of moles, respectively. The molar concentrations are given by $\boldsymbol{c} = \boldsymbol{n}/V$. A model similar to Eq. 1 can be derived for biotechnological reaction systems by expressing the material balances and the continuity equation in mass units; $\boldsymbol{K}$ then represents the matrix of yield coefficients.

Without loss of generality, it is assumed that the time profiles of the inlet flow rates $\boldsymbol{q}_{\text{in}}$ are linearly independent and the inlet molar concentrations $\boldsymbol{c}_{\text{in}}^i$ $(i = 1, \ldots, p)$ are constant (see section on varying inlet concentrations). Finally, note that the outlet flow rate q_{out} does not necessarily depend on $\boldsymbol{q}_{\text{in}}$.

Transformation to Normal Form

Reaction invariants in the absence of inlets and outlets

The aim here is the extension of the concept of reaction invariants to obtain a normal form for chemical-reaction systems. As a first step toward understanding reaction invariants, a chemical-reaction system with neither inlet nor outlet streams is considered:

$$\dot{\boldsymbol{n}} = V\boldsymbol{K}\boldsymbol{r}_n(\boldsymbol{n},V), \qquad \mathbf{n}(0) = \boldsymbol{n}_0,$$
$$\dot{V} = 0, \qquad V(0) = V_0. \quad (2)$$

Though there are $(S+1)$ differential equations in Eq. 2, it is shown below that the reaction system has intrinsically only R states or directions in which $\boldsymbol{n}$ evolves with time, since there are only R independent reactions. The other $(S-R)$ directions are unaffected by the reactions, and are termed the *invariants of the reaction system* (Waller and Mäkilä, 1981).

The state space will be separated into (1) an R-dimensional vector space that evolves due to the R independent reactions (the *reaction variants*), and (2) the $(S-R)$ dimensional reaction invariants. The ideas of Moore–Penrose pseudoinverse (denoted by superscript $+$) and completion of space will be used for this purpose. Let $\boldsymbol{P} \in \mathbb{R}^{S \times (S-R)}$ be a matrix with orthonormal columns that satisfies (1) rank $([\boldsymbol{K}, \boldsymbol{P}]) = S$, and (2) $\boldsymbol{P}^T\boldsymbol{K} = \boldsymbol{0}_{(S-R)\times R}$. Then, the *linear* transformation that separates the R-dimensional reaction variants, z_1, and the $(S-R)$-dimensional reaction invariants, z_2, is given by

$$\begin{bmatrix} z_1 \\ z_2 \end{bmatrix} = \begin{bmatrix} \boldsymbol{K}^+\boldsymbol{n} \\ \boldsymbol{P}^T\boldsymbol{n} \end{bmatrix}. \quad (3)$$

Substituting Eq. 3 in Eq. 2 and using $\boldsymbol{r}_z(z,V)$ for the reaction rates in the new coordinates gives

$$\dot{z}_1 = V\boldsymbol{r}_z(z,V), \qquad z_1(0) = \boldsymbol{K}^+\boldsymbol{n}_0,$$
$$\dot{z}_2 = \boldsymbol{0}_{S-R}, \qquad z_2(0) = \boldsymbol{P}^T\boldsymbol{n}_0,$$
$$\dot{V} = 0, \qquad V(0) = V_0. \quad (4)$$

Remark 1 (Construction of P). Note that the columns of $\boldsymbol{P}$ span the null space of $\boldsymbol{K}^T$. Therefore, one way to construct $\boldsymbol{P}$ is by singular value decomposition (SVD) of $\boldsymbol{K}$ (Golub and Van Loan, 1983). $\boldsymbol{P}$ is the matrix of the right singular vectors corresponding to the zero singular values of $\boldsymbol{K}$.

Reaction invariants in the presence of inlets and outlets

Even when inlets and outlets are present, the reactions affect only an R-dimensional space. The reaction invariants can be separated using the transformation Eq. 3. Applying Eq. 3 to Eq. 1 gives

$$\dot{z}_1 = V\boldsymbol{r}_z(z,V) + \boldsymbol{K}^+\boldsymbol{C}_{\text{in}}\boldsymbol{q}_{\text{in}} - (q_{\text{out}}/V)z_1, \qquad z_1(0) = \boldsymbol{K}^+\boldsymbol{n}_0,$$
$$\dot{z}_2 = \boldsymbol{P}^T\boldsymbol{C}_{\text{in}}\boldsymbol{q}_{\text{in}} - (q_{\text{out}}/V)z_2, \qquad z_2(0) = \boldsymbol{P}^T\boldsymbol{n}_0,$$
$$\dot{V} = \left(\boldsymbol{1}_p^T\boldsymbol{q}_{\text{in}}\right) - q_{\text{out}}, \qquad V(0) = V_0. \quad (5)$$

Note that, though z_2 and V are reaction invariants, they do not remain constant. Thus, the evolution of $\boldsymbol{n}$ is no longer restricted to an R-dimensional space, as previously; it evolves in a larger space. A similar conclusion has been drawn by Fjeld et al. (1974).

In the absence of inlets and outlets, isolating the manifold in which $\boldsymbol{n}$ evolves and spotting the reaction invariants are the same problem. This is because the variation in $\boldsymbol{n}$ is caused only through the R independent reactions. Alternatively, in the presence of inlets and outlets, the variation in $\boldsymbol{n}$ and V is not only due to reactions but also due to flows (inlets and outlets). Thus, isolating the manifold in which $\boldsymbol{n}$ and V evolve means finding and eliminating states that are invariant with respect to both reactions and flows.

Reaction and flow invariants

The key aim of this article is to provide a three-part decomposition of the system equations (Eqs. 1). The first part is that which is affected by the R independent reactions. Among the reaction invariants, the second part picks those states that evolve with the flows. The third part consists of those states that remain constant, that is, reaction *and* flow invariants. Note that the transformation to normal form that is proposed to this effect is *nonlinear*.

The dimension of the reaction variant space is R. As will be seen below, the dimension of the manifold in which the transformed states evolve is given by $\sigma + 1$, where $\sigma \equiv$ rank $([\boldsymbol{K}, \boldsymbol{C}_{\text{in}}])$. This means that the dimension increases with every inlet whose molar concentrations are independent of both

K and the remaining inlet molar concentrations. First, it is assumed that $\sigma = R + p$. It will be shown that the dimension of the reaction variant space is R, that of the reaction invariant and flow variant space are $p + 1$, and that of the reaction and flow invariant space are $S - \sigma$. Next, the transformation to normal form will be developed, and it will then be generalized to the case of $\sigma < R + p$.

In comparison with Eq. 3, the completion of the state space involving n and V takes a three-level structure. Let $L \in \mathbb{R}^{S \times (\sigma - R)}$ and $N \in \mathbb{R}^{S \times (S - \sigma)}$ be matrices with orthonormal columns that satisfy the following conditions: (1) rank ($[K, L, N]) = S$; (2) K, L, and N are mutually orthogonal; (3) $N^T C_{\text{in}} = 0_{S - \sigma \times p}$; (4) $L^T C_{\text{in}}$ is invertible.

For the application of the three-part decomposition, the transformation to normal form (Eq. 3) has to be changed as follows: (1) instead of P, an $S \times (\sigma - R)$ matrix, M, has to be chosen that renders $M^T C_{\text{in}} = I_{(\sigma - R)}$, achieved by choosing $M \equiv L(C_{\text{in}}^T L)^{-1}$; and (2) $K^+ C_{\text{in}} q_{\text{in}}$ has to be eliminated. For this, an additional projection matrix $(I_S - C_{\text{in}} M^T)$ is formulated which, by construction of M, satisfies $(I_S - C_{\text{in}} M^T) K = K$. With these modifications, the transformation to normal form reads:

$$\begin{bmatrix} z_1 \\ z_2 \\ z_3 \end{bmatrix} = \begin{bmatrix} K^+ (I_S - C_{\text{in}} M^T) n \\ M^T n \\ N^T n \end{bmatrix} \tag{6}$$

and

$$\begin{aligned} \dot{z}_1 &= V r_z(z, V) - (q_{\text{out}}/V) z_1, & z_1(0) &= K^+ (I_S - C_{\text{in}} M^T) n_0, \\ \dot{z}_2 &= q_{\text{in}} - (q_{\text{out}}/V) z_2, & z_2(0) &= M^T n_0, \\ \dot{z}_3 &= -(q_{\text{out}}/V) z_3, & z_3(0) &= N^T n_0, \\ \dot{V} &= \left(1_p^T q_{\text{in}}\right) - (q_{\text{out}}/V) V, & V(0) &= V_0, \end{aligned} \tag{7}$$

where z_1, z_2, and z_3 are vectors of dimension R, p, and $(S - \sigma)$, respectively. For the elimination of the term related to (q_{out}/V), a *nonlinear* transformation can be used:

$$\begin{bmatrix} x \\ \nu \end{bmatrix} = \begin{bmatrix} z/\left(V - 1_p^T z_2\right) \\ V - 1_p^T z_2 \end{bmatrix}, \tag{8}$$

where x and ν are the transformed states of dimensions $(R + S + p - \sigma)$ and 1, respectively. By introducing a nonzero scaling factor η, the following theorem, which formulates the so-called *normal form* of Eq. 1, is proposed.

Theorem 2. Let $\sigma = \text{rank}\ ([K, C_{\text{in}}]) = (R + p)$. Then, a diffeomorphism $\mathfrak{T}$: $\left[\begin{smallmatrix} n \\ V \end{smallmatrix}\right] \leftrightarrow \left[\begin{smallmatrix} x \\ \nu \end{smallmatrix}\right]$ exists that transforms model Eq. 1 into

$$\begin{aligned} \dot{x}_1 &= h(x_2) r(x), & x_1(0) &= g_0 K^+ (I_S - C_{\text{in}} M^T) n_0, \\ \dot{x}_2 &= q_{\text{in}}/\nu, & x_2(0) &= g_0 M^T n_0, \\ \dot{x}_3 &= 0_{S - \sigma}, & x_3(0) &= g_0 N^T n_0, \\ \dot{\nu} &= -q_{\text{out}}/h(x_2), & \nu(0) &= 1/g_0, \end{aligned} \tag{9}$$

where

$$\begin{aligned} h(x_2) &= \eta + 1_p^T x_2, \\ g_0 &= \eta/\left(V_0 - 1_p^T M^T n_0\right), \end{aligned} \tag{10}$$

and x_1, x_2, and x_3 are vectors of dimension R, p, and $(S - \sigma)$, respectively; η a nonzero arbitrary constant; r the R-dimensional reaction-rate vector expressed in terms of x, $M = L(C_{\text{in}}^T L)^{-1}$, $L \in \mathbb{R}^{S \times (\sigma - R)}$, and $N \in \mathbb{R}^{S \times (S - \sigma)}$ matrices with orthonormal columns that satisfy: (1) rank ($[K, L, N]) = S$; (2) K, L, and N are mutually orthogonal; (3) $N^T C_{\text{in}} = 0_{S - \sigma \times p}$; and (4) $L^T C_{\text{in}}$ is invertible.

The transformation to normal form is one-to-one and can be written as follows, using $g(n, V) = \eta/(V - 1_p^T M^T n)$:

$$\begin{bmatrix} n \\ V \end{bmatrix} \rightarrow \begin{bmatrix} x \\ \nu \end{bmatrix} : \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ \nu \end{bmatrix} \begin{bmatrix} g(n, V) K^+ (I_S - C_{\text{in}} M^T) n \\ g(n, V) M^T n \\ g(n, V) N^T n \\ 1/g(n, V) \end{bmatrix} \tag{11}$$

$$\begin{bmatrix} x \\ \nu \end{bmatrix} \rightarrow \begin{bmatrix} n \\ V \end{bmatrix} : \begin{bmatrix} n \\ V \end{bmatrix} = \begin{bmatrix} \nu (K x_1 + C_{\text{in}} x_2 + N x_3) \\ \nu h(x_2) \end{bmatrix}. \tag{12}$$

(see Appendix A for proof). The matrices N and L required in Theorem 2 can be constructed in a similar way to Remark 1 by noting that the columns of N and L span the null spaces of $[K, C_{\text{in}}]^T$ and $[K, N]^T$, respectively.

Theorem 2 can be easily extended to the case where $\sigma < R + p$. For this, the matrix M is redefined using the pseudoinverse of $(C_{\text{in}}^T L)$ instead of the inverse such that $M := L(C_{\text{in}}^T L)^+$. It will be shown that the transformation to normal form in this case is no longer one-to-one.

Corollary 3. For $\sigma < R + p$, the transformed model (Eq. 9) represents Eq. 1, where $M = L(C_{\text{in}}^T L)^+$. The relation $\left[\begin{smallmatrix} x \\ \nu \end{smallmatrix}\right] \rightarrow \left[\begin{smallmatrix} n \\ \nu \end{smallmatrix}\right]$ is defined by Eq. 12 (see Appendix B for proof).

Discussion

The results obtained in Theorem 2 and Corollary 3 are summarized in Table 1. Although a rigorous interpretation of the results is difficult due to the nonlinear term in the transformation to normal form, an intuitive meaning for the various parts of x can be given. The R-dimensional reaction variants are described by x_1, while x_2 captures the p-dimen-

Table 1. Transformation to Normal Form

Orig. Space	React. Var.	React. Invar. and Flow Var. (Inlet)	React. and Flow Invar.	React. Invar. and Flow Var. (Outlet)
	x_1	x_2	x_3	ν
	$\dot{x}_1 = h(x_2) r(x)$	$\dot{x}_2 = q_{\text{in}}/\nu$	$\dot{x}_3 = 0$	$\dot{\nu} = -q_{\text{out}}/h(x_2)$
$n =$	$(K x_1$ +	$C_{\text{in}} x_2$ +	$N x_3)$	ν
$V =$		$h(x_2)$		ν
$c =$	$(K x_1$ +	$C_{\text{in}} x_2$ +	$N x_3)$	
		$h(x_2)$		
$\mathbb{R}^{S+1}$	$\mathbb{R}^R$	$\mathbb{R}^p$	$\mathbb{R}^{(S - \sigma)}$	$\mathbb{R}^1$

sional flow part. The $(S-\sigma)$-dimensional reaction and flow invariants are x_3, with ν being related to the outflow.

The third row depicts the differential equations that explain why the interpretation of the states outlined earlier is possible. The fourth and fifth rows summarize the reconstruction of the original states $\boldsymbol{n}$ and V. With this transformation to normal form, $\boldsymbol{c}$ (sixth row) and $\boldsymbol{n}$ are decomposed along the directions determined by the columns of (1) the stoichiometric matrix $\boldsymbol{K}$; (2) the inlet concentration matrix $\boldsymbol{C}_{\text{in}}$; and (3) the reaction and flow invariant matrix $\boldsymbol{N}$. Note that, in contrast to $\boldsymbol{n}$, $\boldsymbol{c}$ is not directly influenced by the outflow through ν.

In the last row, the dimensions of the various spaces are given. The transformed system is of dimension $(S+R+p-\sigma+1)$, whereas the original system has dimension $(S+1)$. Thus, if $\sigma<(R+p)$, there is an increase in dimension as a result of the transformation to normal form. This is why the transformation to normal form is not one-to-one when $\sigma<(R+p)$. An example is now given as illustration.

Example 4. Consider a reaction system with two independent reactions $(R=2)$: $A\rightarrow B$, $B+C\rightarrow D$. When A and B are fed as two different inlets $(p=2)$, then

$$[\boldsymbol{K}\,\boldsymbol{C}_{\text{in}}]=\begin{bmatrix}-1 & 0 & c_{\text{in},A} & 0\\ 1 & -1 & 0 & c_{\text{in},B}\\ 0 & -1 & 0 & 0\\ 0 & 1 & 0 & 0\end{bmatrix}$$

and $\sigma=3<4=R+p$. This is due to the fact that feeding A along with the reaction $A\rightarrow B$ is equivalent to feeding B. This redundancy is reflected in the loss of rank in $[\boldsymbol{K},\,\boldsymbol{C}_{\text{in}}]$.

Owing to redundancy, a clear separation of the influence of reactions and flows is no longer possible. One way to handle this is to explain the same effect by more than one state, thus artificially increasing the dimension of the state space (see Table 1).

Note that $\boldsymbol{x}_2$ and ν form the flow variant space. However, since ν enters nonlinearly in the reconstruction of $\boldsymbol{n}$ and V, it is given a special symbol. Owing to the redundancy described before, among the $(p+1)$ states present in $[\begin{smallmatrix}x_2\\ \nu\end{smallmatrix}]$ only $(\sigma-R+1)$ states constitute the reaction-invariant and flow-variance space.

Implications of the Transformation to Normal Form

The transformation to normal form for reaction systems with *independent inlet and outlet streams* proposed in the previous section clearly shows the evolution of $\boldsymbol{n}$ in three different spaces: the stoichiometric space $(\boldsymbol{K})$, the inlet space $(\boldsymbol{C}_{\text{in}})$, and the invariant space $(\boldsymbol{N})$. Such a separation has immediate implications for model reduction, state accessibility, state reconstruction, feedback linearizability, and the construction of the linearizing feedback.

Model reduction

From Eq. 9, it is clear that only $(R+p+1)$ differential equations need to be integrated to compute the trajectories. In addition, a set of $(S-\sigma)$ constants must be computed from the initial conditions. In the case of $S>(R+p)$, analysis and design of controllers, observers and optimizers can be achieved with the reduced model of $(R+p+1)$ states if the initial conditions $\boldsymbol{n}_0$ and V_0 are assumed to be known.

State accessibility

It is obvious from the transformation to normal form in Theorem 2 that (1) $\boldsymbol{x}_3$ is inaccessible, and (2) $\boldsymbol{x}_2$ and ν are accessible from the inlet and outlet streams. Moreover, a part of $\boldsymbol{x}_1$ can be inaccessible depending on the kinetics. Thus, the dimension of the inaccessible part is at least $(S-\sigma)$, which leads to the following corollary.

Corollary 5. The maximum dimension of the accessible part is $(\sigma+1)$, where $\sigma=\text{rank}\,([\boldsymbol{K},\,\boldsymbol{C}_{\text{in}}])$.

Therefore, if full state accessibility is required, the dimension of $\boldsymbol{x}_3$ should be zero (i.e., $\sigma=S$), implying that the number of inlet streams should be at least $(S-R)$ (i.e., $p\geq S-R$).

Corollary 6. $\sigma=S$ and $p\geq S-R$ are necessary conditions for full state accessibility.

These results have been reported previously by Bastin and Lévine (1993). However, deriving them from the transformation to normal form in Theorem 2 provides an alternate proof.

Another interesting aspect of the transformation to normal form is that the dynamics of the inaccessible part can be transformed to $\dot{\boldsymbol{x}}_3=\boldsymbol{0}_{S-\sigma}$, which is marginally stable.

State reconstruction

The reconstruction of $\boldsymbol{n}$ as in Eq. 12 can be used to reconstruct the complete state information from a subset of measured molar concentrations. The key idea is that $\boldsymbol{x}_2$, $\boldsymbol{x}_3$, and ν can be calculated at any point from the initial conditions and the flows without knowledge of the kinetics, since they are reaction invariants. Then, if the molar concentrations, $\boldsymbol{c}_s$, of $S_s\geq R$ species are measured, $\boldsymbol{x}_1$ can be calculated under certain minor assumptions. When $\boldsymbol{x}_1$ is available, the number of moles $\boldsymbol{n}$, and also the molar concentration vector $\boldsymbol{c}=\boldsymbol{n}/V$, can be reconstructed from Eq. 12. The idea is similar to that of the asymptotic observer proposed by Bastin and Dochain (1990).

Proposition 7. Let the molar concentrations of $S_s\geq R$ species be measured and $\boldsymbol{K}_s$ be the $S_s\times R$ submatrix of $\boldsymbol{K}$ corresponding to these S_s species. Given $\boldsymbol{K}$, $\boldsymbol{C}_{\text{in}}$, q_{in}, q_{out}, $\boldsymbol{c}_0$, and V_0, if $\boldsymbol{K}_s$ has a unique left pseudoinverse, the molar concentrations of the remaining $(S-S_s)$ species, $\boldsymbol{c}_t$, can be reconstructed without knowledge of reaction kinetics using

$$\boldsymbol{c}_t=\boldsymbol{K}_t\boldsymbol{K}_s^{+}\boldsymbol{c}_s+(\boldsymbol{C}_{\text{in},t}-\boldsymbol{K}_t\boldsymbol{K}_s^{+}\boldsymbol{C}_{\text{in},s})\boldsymbol{x}_2/h(\boldsymbol{x}_2)+(\boldsymbol{N}_t-\boldsymbol{K}_t\boldsymbol{K}_s^{+}\boldsymbol{N}_s)\boldsymbol{x}_3/h(\boldsymbol{x}_2),\quad(13)$$

where the subscript s represents a quantity corresponding to the measured S_s molar concentrations and t to that of the $(S-S_s)$ unmeasured molar concentrations.

Let only an estimate of the initial molar concentrations of the S_t species be available. Then the estimation error $\boldsymbol{e}\equiv\hat{\boldsymbol{c}}_t-\boldsymbol{c}_t$, with $\hat{\boldsymbol{c}}_t$ being the estimated molar concentrations, is given by

$$\boldsymbol{e}=\frac{h(\boldsymbol{x}_2(0))}{h(\boldsymbol{x}_2)}\boldsymbol{e}(0).\quad(14)$$

If at least one of the inlet flow rates is always nonzero, then the estimated molar concentrations $\hat{c}_t$ asymptotically converge to the true molar concentrations c_t (see Appendix C for proof).

The asymptotic convergence can intuitively be explained from Eq. 14. The numerator term is constant, while the denominator monotonically increases if at least one of the inlet flow rates is always nonzero. $h(x_2)$ tends to infinity with time, thereby pushing the error to zero. Since the estimation errors of the S_t species are independent of each other, an initial molar concentration error of any species does not propagate on the molar concentration estimates of the remaining species.

It can be seen from Eq. 14 that the error e tends to zero only due $h(x_2)$ going to infinity. Thus, since $h = V/\nu$, either the volume goes to infinity or ν goes to zero. Both imply that an infinite dilution is necessary to make the estimation independent of the initial concentrations.

However, if molar concentrations of fewer than R species are measured, then observer techniques relying on the knowledge of reaction kinetics should be used (Soroush, 1997).

Feedback linearizability

Consider a reduced system that does not include the inaccessible part x_3. The system is affine in the inputs and is given by

$$\dot{x} = \left[\begin{array}{c} \dot{x}_1 \\ \hline \dot{x}_2 \\ \hline \dot{\nu} \end{array}\right] = \left[\begin{array}{c} f_1(x) \\ \hline \mathbf{0}_p \\ \hline 0 \end{array}\right] + \left[\begin{array}{c|c} \multicolumn{2}{c}{\mathbf{0}_{R\times m}} \\ \hline (1/\nu)I_p & \mathbf{0}_p \\ \hline \mathbf{0}_p^T & -1/h(x_2) \end{array}\right] u$$

$$\equiv f(x) + \sum_{j=1}^{m} g_j u_j, \quad u = \begin{bmatrix} q_{\text{in}} \\ q_{\text{out}} \end{bmatrix} \tag{15}$$

where f and g_j are n-dimensional vector fields, f_1 is an R-dimensional vector field, and u the m-dimensional input vector. m and n are the dimensions of u and x, respectively, with, in this case, $m = (p+1)$ and $n = (R+m)$. Owing to the special structure of the vector fields, important results regarding the feedback linearizability of Eq. 14 can be obtained. A system is feedback linearizable if a state feedback and a diffeomorphism exist, which renders the closed-loop system linear (see Appendix D for conditions of feedback linearizability).

Proposition 8. Given Eq. 15 with $\sigma = (R+p)$ and $m \geq R$ inputs, if the $R \times m$ matrix $J = [(1/\nu)\,(\partial f_1/\partial x_2),\, (-1/h(x_2))\,(\partial f_1/\partial \nu)]$ is of rank R, then Eq. 15 is feedback linearizable (see Appendix D for proof).

An advantage of model (1) transformed into Eq. 14 is that the linearizing feedback can be calculated easily. With this feedback, the system is linear—no further diffeomorphism is required.

Since x_1 and a part of x_2 form the flat outputs (Fliess et al., 1995), linearization of Eq. 14 to $\ddot{x}_1 = v_u$ and $\dot{x}_{2,\upsilon} = v_\upsilon$ with the new external inputs $v_u \in \mathbb{R}^R$ and $v_\upsilon \in \mathbb{R}^{m-R}$ can be achieved, where $x_2 = \left[\begin{smallmatrix} x_{2,u} \\ x_{2,\upsilon} \end{smallmatrix}\right]$. Differentiating $\dot{x}_1$ with respect to time,

$$v_u = \ddot{x}_1 = \frac{\partial f_1}{\partial x_1} f_1 + Ju. \tag{16}$$

Partitioning $J = [J_s, J_t]$ such that $J_s \in \mathbb{R}^{R\times R}$ is invertible, the following feedback is computed from Eq. 16:

$$u = \begin{bmatrix} -J_s^{-1} \dfrac{\partial f_1}{\partial x_1} f_1 \\ \mathbf{0}_{m-R} \end{bmatrix} + \begin{bmatrix} J_s^{-1} & -J_s^{-1}J_t \\ \mathbf{0}_{(m-R)\times R} & I_{m-R} \end{bmatrix} \begin{bmatrix} v_u \\ v_\upsilon \end{bmatrix}. \tag{17}$$

Note that $(m-R)$ inputs are superfluous and are thus not necessary to control the R reactions.

The assumption of full rank for J is not very restrictive, especially when only independent reactions are considered. If only nonreacting species are added, it is clear that they will not affect the reaction rates, and J will lose rank. In contrast, if different reacting species in at least R inlets are fed to the reaction system, the assumption of full rank for J can be met easily.

In the preceding proposition, only sufficient conditions for full-state feedback linearizability have been provided. An example illustrating the conservatism of these conditions is given next. The semibatch reaction system $A + B \rightarrow C$ and $A + C \rightarrow D$ with second-order kinetics and B being fed ($m = p = 1$, $R = 2$). Although the conditions of Proposition 8 are not verified, it can easily be verified that the system is feedback-linearizable.

Extensions to Other Types of Reaction Systems

The transformation to normal form was stated in the section titled "Transformation to Normal Form" for reaction systems with constant temperature, density, and inlet molar concentrations. Below, these results are extended to cover practical situations commonly found in chemical reaction systems, in particular those dealing with varying temperature, density and inlet molar concentrations.

Nonisothermal reaction systems

In a nonisothermal scenario, the temperature, T, should be modeled as an additional state. Under the assumptions that (1) the pressure and the density remain constant, (2) the mixing enthalpies are negligible, and (3) the temperatures, T_{in}, of the p inlet streams remain constant, the heat-balance equation is

$$\frac{d}{dt}(V\rho c_p T) = V(-\Delta h_R^T) r_n(n, V, T) + T_{\text{in}}^T S_{\text{in}} \Phi_{\text{in}} q_{\text{in}}$$
$$-(q_{\text{out}}/V)(V\rho c_p T) + Q_{\text{ext}}, \tag{18}$$

where Δh_R is the R-dimensional vector of reaction enthalpies; c_p the specific heat capacity; ρ the density of the mixture; S_{in} and Φ_{in} p-dimensional diagonal matrices with elements being the specific heat capacities and densities of the inlet streams, respectively; and Q_{ext} the external heat energy such as external heating/cooling energy or heat dissipation. Using $T^\star = \rho c_p T$, the model for nonisothermal constant density reaction systems is given by

$$
\begin{aligned}
\dot{\boldsymbol{n}} &= V\boldsymbol{K}\boldsymbol{r}_n(\boldsymbol{n},V,T^\star)+\boldsymbol{C}_{\text{in}}\boldsymbol{q}_{\text{in}}-(q_{\text{out}}/V)\boldsymbol{n}, && \boldsymbol{n}(0)=\boldsymbol{n}_0,\\
\frac{d}{dt}(VT^\star) &= V(-\Delta\boldsymbol{h}_R^T)\boldsymbol{r}_n(\boldsymbol{n},V,T^\star)+\boldsymbol{T}_{\text{in}}^{\star T}\boldsymbol{q}_{\text{in}}-(q_{\text{out}}/V)(VT^\star)+Q_{\text{ext}}, && T^\star(0)=T_0^\star, \quad (19)\\
\dot{V} &= \left(\boldsymbol{1}_p^T\boldsymbol{q}_{\text{in}}\right)-q_{\text{out}}, && V(0)=V_0.
\end{aligned}
$$

Furthermore, it is assumed that $\boldsymbol{S}_{\text{in}}$ and $\boldsymbol{\Phi}_{\text{in}}$ are constant. For the formulation of the transformation of Eq. 19 into normal form, the heat balance equation is not transformed when the external energy is nonnegligible ($Q_{\text{ext}} \neq 0$). However, the remaining equations are transformed using Eq. 9, since the transformation to normal form proposed in Theorem 2 is independent of reaction kinetics and temperature. Note that the dimension of the inaccessible part $\boldsymbol{x}_3$ does not decrease even when the temperature is used as an additional input for control.

When $Q_{\text{ext}} = 0$, then $(VT^\star)$ can be combined with $\boldsymbol{n}$ leading to

$$
\frac{d}{dt}\begin{bmatrix}\boldsymbol{n}\\(VT^\star)\end{bmatrix} = V\begin{bmatrix}\boldsymbol{K}\\-\Delta\boldsymbol{h}_R^T\end{bmatrix}\boldsymbol{r}_n(\boldsymbol{n},V,T^\star) + \begin{bmatrix}\boldsymbol{C}_{in}\\\boldsymbol{T}_{in}^{\star T}\end{bmatrix}\boldsymbol{q}_{\text{in}} - (q_{\text{out}}/V)\begin{bmatrix}\boldsymbol{n}\\(VT^\star)\end{bmatrix}. \quad (20)
$$

From Eq. 20 the state $(VT^\star)$ can be modeled as an additional species and, hence, $S_T \equiv S+1$. If σ = rank $([\boldsymbol{K},\boldsymbol{C}_{\text{in}}]) = R+p$, then rank

$$
\left(\begin{bmatrix}\boldsymbol{K} & \boldsymbol{C}_{\text{in}}\\ -\Delta\boldsymbol{h}_R^T & \boldsymbol{T}_{\text{in}}^{\star T}\end{bmatrix}\right) = R+p.
$$

Since $(S_T+\sigma) = (S-\sigma)+1$, the number of reaction and flow invariants (inaccessible states) is increased by 1. This means that the additional state $(VT^\star)$ is inaccessible in the absence of external heating. Intuitively, the temperature cannot vary independently of the reactions and the flows without external heating since the evolution of the reactions is already captured by $\boldsymbol{n}$.

Varying-density reaction systems

In reaction systems with constant density ρ, the conservation equation for total mass, m, translates directly into a conservation equation for the volume V, as was the case in Eq. 1. This is due to the relationship $V = m/\rho$, with ρ being constant. In the case of varying density, however, the mass conservation leads to

$$
\frac{d}{dt}(\rho V) = \boldsymbol{1}_p^T\boldsymbol{\Phi}_{\text{in}}\boldsymbol{q}_{\text{in}} - \rho q_{\text{out}}, \qquad (\rho V)(0) = \rho_0 V_0. \quad (21)
$$

In the case of varying density, $\dot{\boldsymbol{n}}$ in Eq. 1 can still be transformed as in Theorem 2 if h is redefined using the following algebra. Substituting $V = h\nu$ in Eq. 21 and using Eq. 9, $(d/dt)(\rho h) = \boldsymbol{1}_p^T\boldsymbol{\Phi}_{\text{in}}(\boldsymbol{q}_{\text{in}}/\nu)$. After integrating both sides, the following redefinition of h results:

$$
h(\boldsymbol{x},\nu) := \left(\boldsymbol{1}_p^T\boldsymbol{\Phi}_{\text{in}}\boldsymbol{x}_2+\eta^\star\right)/\rho(\boldsymbol{x},\nu), \quad (22)
$$

where $\eta^\star$ is an arbitrary integration constant. An important difference between the original definition (Eq. 10) and the redefinition (Eq. 22) is that, since ρ depends on both $\boldsymbol{x}$ and ν, the redefined h depends not only on $\boldsymbol{x}_2$ but also on ν and the *entire* $\boldsymbol{x}$ vector. Note that since $g = h(\boldsymbol{x},\nu)/V$, it gets redefined as $g(\boldsymbol{n},V) := \eta^*/(\rho V - \boldsymbol{1}_\rho^T\Phi_{\text{in}}\boldsymbol{M}^T\boldsymbol{n})$.

Since $\boldsymbol{\Phi}_{\text{in}}$ is assumed to be constant and is usually available, availability of the inlet volumetric flow rates $\boldsymbol{q}_{\text{in}}$ and the inlet mass flow rates $\boldsymbol{u}_{\text{in}} = \boldsymbol{\Phi}_{\text{in}}\boldsymbol{q}_{\text{in}}$ is equivalent. Since the varying density ρ is usually unknown, however, the outlet mass flow rate, $u_{\text{out}} = \rho q_{\text{out}}$, cannot be calculated from q_{out} and *vice versa*.

If u_{out} is available, then $\dot{\nu}$ in the transformed system (Eq. 9) has to be replaced by

$$
\begin{aligned}
\dot{\nu} = -q_{\text{out}}/h(\boldsymbol{x},\nu) &= -q_{\text{out}}\,\rho/\left(\boldsymbol{1}_p^T\boldsymbol{\Phi}_{\text{in}}\boldsymbol{x}_2+\eta^\star\right)\\
&= -u_{\text{out}}/\left(\boldsymbol{1}_p^T\boldsymbol{\Phi}_{\text{in}}\boldsymbol{x}_2+\eta^*\right). \quad (23)
\end{aligned}
$$

In this case, ν, and hence $\boldsymbol{x}_2$ (see Eq. 9), are independent of ρ, which implies that ν and $\boldsymbol{x}_2$ are reaction invariants. Note that h is as defined in Eq. 22.

In summary, the structure of the transformed system (Eq. 9) is retained for varying-density reaction systems except for the redefinition of h. With volumetric flow rates, the interpretation of the three-part decomposition discussed in the subsection titled "Discussion" is not possible due to coupling through the density. Alternatively, if the mass flow rates are available, the interpretation of the three-part decomposition is still valid, since ν and $\boldsymbol{x}_2$ are independent of the density.

Varying inlet concentrations

Consider the case where $\boldsymbol{C}_{\text{in}}$ is time-varying. The transformation to normal form is carried out in two steps. In the first step, the system with inlet streams of *varying* inlet molar concentrations is transformed into one with inlet streams of *constant* inlet molar concentrations. The second step is the transformation to normal form, which has been discussed in earlier sections.

For the first step, let the $S \times K$ matrix $\boldsymbol{F}_{\text{in}}$, and the $p \times K$ matrix $\boldsymbol{Q}_{\text{in}}$ be defined as

$$
\begin{aligned}
\boldsymbol{F}_{\text{in}} &\equiv [\boldsymbol{C}_{\text{in}}(0)\boldsymbol{q}_{\text{in}}(0),\ldots,\boldsymbol{C}_{\text{in}}(K-1)\boldsymbol{q}_{\text{in}}(K-1)],\\
\boldsymbol{Q}_{\text{in}} &\equiv [\boldsymbol{q}_{\text{in}}(0),\ldots,\boldsymbol{q}_{\text{in}}(K-1)], \quad (24)
\end{aligned}
$$

where K is the number of time discretization points. Let $f \equiv$ rank $(\boldsymbol{F}_{\text{in}})$. $\boldsymbol{F}_{\text{in}}$ can be decomposed using, for example, SVD such that $\boldsymbol{F}_{\text{in}} = \overline{\boldsymbol{C}}_{\text{in}}\overline{\boldsymbol{Q}}_{\text{in}}$, where $\overline{\boldsymbol{C}}_{\text{in}}$ and $\overline{\boldsymbol{Q}}_{\text{in}}$ are the $S \times f$ matrix of constant inlet molar concentrations and the $f \times K$ matrix of corresponding inlet volumetric flow rates for K discretization points, respectively. The $S \times (f+1)$ constant inlet molar concentration matrix C^*_{in} and the $(f+1)\times K$ matrix of flow rates, Q^*_{in}, are defined as

$$C^*_{in} \equiv [\bar{C}_{in}\ \ 0_S], \quad Q^*_{in} \equiv \begin{bmatrix} \bar{Q}_{in} \\ 1^T_p Q_{in} - 1^T_f \bar{Q}_{in} \end{bmatrix}. \tag{25}$$

The $(f+1)$-dimensional inlet volumetric flow rate vector $q^*_{in}(k)$ at the kth discretization instant is the $(k+1)$th column of Q^*_{in} $(k = 0, \ldots, K-1)$. f represents the number of the species that can be independently manipulated by the inlet streams. The addition of one comes from the fact that the volume can be influenced by time-varying inlet molar concentrations. If $1^T_p Q_{in} - 1^T_f \bar{Q}_{in} = 0$, which is the case when C_{in} is constant, the addition of one does not apply. With definition (Eq. 25)

$$C_{in}(k) q_{in}(k) = \bar{C}_{in} \bar{q}_{in}(k) = C^*_{in} q^*_{in}(k),$$
$$1^T_p q_{in}(k) = 1^T_{f+1} q^*_{in}(k). \tag{26}$$

Substituting Eq. 26 in Eq. 1 leads to

$$\dot{n} = VKr(c) + C^*_{in} q^*_{in} - (q_{out}/V) n, \qquad n(0) = n_0$$
$$\dot{V} = 1^T_{f+1} q^*_{in} - q_{out}, \qquad V(0) = V_0. \tag{27}$$

Redefining $C_{in} := C^*_{in}$, $q_{in} := q^*_{in}$, and $p := f+1$, it follows that Eq. 27 is equivalent to Eq. 1. Thus, the structure of the reaction system in normal form (Eq. 9) is retained even for reaction systems with varying inlet concentrations except for redefinition of the inlet streams. Also, the interpretation of the three-part decomposition is valid.

Special Cases

In the development of the transformation to normal form in the third section, it was assumed that the inlets and outlets are independent. In certain important special cases, however, q_{out} is not independent, for example, for (1) semibatch reaction systems, where $q_{out} = 0$, and (2) CSTRs where $q_{out} = 1^T_p q_{in}$. That this dependence leads to inaccessibility of the volume since the outflow loses its direct influence on the volume is shown next.

Semibatch reaction systems

Owing to the absence of an outlet stream, $\dot{v} = 0$, implying $v(t) = v_0$. Thus, $V = v_0 h(x_2)$. The transformed set of equations is given below:

$$\dot{x}_1 = h(x_2) r(x), \quad \dot{x}_2 = q_{in}/v_0, \quad \dot{x}_3 = 0_{S-\sigma}, \quad \dot{v} = 0. \tag{28}$$

Note that the transformation given by Eqs. 11–12 is linear since $g(n,V)$ is a constant with $g(n,V) = 1/v_0$.

Continuous stirred-tank reaction systems

In a CSTR, $q_{out} = 1^T_p q_{in}$, $\dot{V} = 0$ and $V(t) = V_0$. Since the nonlinear transformation (Eq. 8) of V to v is not required to get to the normal form, a similar transformation as in Eq. 3 can be used to obtain the transformed system:

$$\dot{x}_1 = h(x_2) r(x), \quad \dot{x}_2 = h(x_2) q_{in}/V_0, \quad x_3 = 0_{S-\sigma}, \quad \dot{V} = 0. \tag{29}$$

As discussed in the subsection "Discussion," the reaction invariant and flow variant space has a maximum dimension of $(\sigma - R + 1)$. In the two special cases just shown, the same quantity is limited to a maximum of p, since there are only p independent flows. Combining these two limits, the dimension of the reaction invariant and flow variant space is determined as $\min(\sigma - R + 1, p)$.

The number of reaction invariants and flow variants $\min(\sigma - R + 1, p)$ equals p for either of the following two cases: (1) $\sigma = (R + p)$, and (2) $\sigma = R + p - 1$. This means that the number of accessible states is not reduced even when the molar concentrations of one inlet stream are dependent on the stoichiometry and the molar concentrations of the remaining inlet streams. Intuitively, this is due to the volume becoming accessible in the case of $\sigma = R + p - 1$, as discussed below.

Addition of solvent

The addition of solvent is considered as an example for $\sigma = R + p - 1$. The inlet molar concentration matrix has the form $C_{in} := [c^1_{in}, \ldots, c^{(p-1)}_{in}, 0_S]$. If it is assumed that rank $([K, c^1_{in}, \ldots, c^{(p-1)}_{in}]) = R + p - 1$, then rank $([K, C_{in}]) = R + p - 1$. Intuitively, when the outlet is dependent on the inlets, the addition of solvent makes the volume accessible, since adding the solvent changes the volume, thereby diluting other species and affecting n and V. Note that, for the tangent-linearized model with no outlet stream and rank $([K, c^1_{in}, \ldots, c^{(p-1)}_{in}]) = R + p - 1$, local controllability of the volume by solvent addition has been proven by Dochain and Chen (1992). However, the work presented herein proposed *global* results for *nonlinear* chemical reaction systems.

Example

The concept of model reduction, state reconstruction, state accessibility, and feedback linearizability is now illustrated on a homogeneous, constant-density, nonisothermal semibatch reaction system ($R = 3$ and $S = 7$), namely the ethanolysis of phthaloyl dichloride (A) (de Vallière, 1989). In two successive irreversible ethanolysis reactions, phthalyl chloride monoethyl ester (C), the desired product, and phthalic diethylester (E) are produced from ethanol (B). Both reactions also produce hydrochloric acid (D). It is assumed that B also reacts with D in a reversible side reaction to produce ethyl chloride (F) and water (G). The reaction system can be described by the following reaction scheme:

$$\begin{aligned} A + B &\xrightarrow{r_1} C + D \\ C + B &\xrightarrow{r_2} E + D \\ D + B &\overset{r_3}{\rightleftharpoons} F + G \end{aligned} \qquad \text{with} \qquad K = \begin{bmatrix} -1 & 0 & 0 \\ -1 & -1 & -1 \\ 1 & -1 & 0 \\ 1 & 1 & -1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 1 \end{bmatrix}.$$

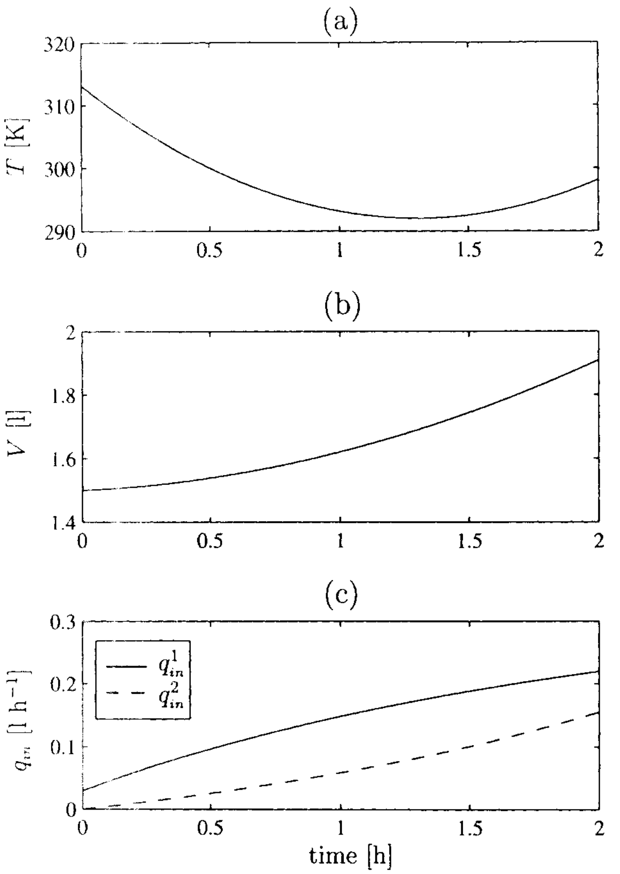

Figure 1. Time profiles of (a) temperature T; (b) volume V; and (c) inlet volumetric flow rates q_{in}.

The molar concentration vector reads $c = [c_A, c_B, c_C, c_D, c_E, c_F, c_G]^T$. Since a known temperature profile $T(t)$ is imposed (see Figure 1a), the differential equation for T can be neglected. Hence, the model is of order 8. The reaction rates are assumed to follow the so-called *mass-action principle*:

$$r_1 = \kappa_1(T)c_Ac_B, \quad r_2 = \kappa_2(T)c_Bc_C,$$
$$r_3 = \kappa_3(T)c_Bc_D - \kappa_4(T)c_Fc_G,$$

with κ_i following the Arrhenius law $\kappa_i(T) = \kappa_{i,0} \exp(-E_i^*/T)$. The numerical values of the parameters are given in Table 2.

Semibatch operation with $p = 2$ inlet streams and no outlet will now be studied with C_{in} chosen such that rank $([K, C_{\text{in}}]) = R + p$. In this way, the transformation to normal form (diffeomorphism) of Theorem 2 can be illustrated. Ethanol (1.5 L with 2 wt. % water) in 80 wt. % solvent (dimethyl sulfoxide) is initially placed in a vessel, that is, $c_0 = [0, 4.2, 0, 0, 0, 0, 0.22]^T$ M. The first inlet stream contains phthaloyl dichloride, and the second an ethanol/water mixture, that is, $c_{\text{in}}^1 = [6.9, 0, 0, 0, 0, 0, 0]^T$ M and $c_{\text{in}}^2 = [0, 17, 0, 0, 0, 0, 1.5]^T$ M. The inlet volumetric flow rate profiles are given in Figure 1c, the volume profile in Figure 1b, and the molar concentration profiles in Figure 2.

Equation 1 can be reduced to $(R + p) = 5$ differential equations as given in Theorem 2. With the choice $\eta \equiv V_0 - \mathbf{1}_p^T M^T n_0 = 1.085$ l, $\nu(t) = \nu_0 = 1$. From Eqs. 12 and 23, the reduced model and the reconstructed molar concentrations c read:

Table 2. Numerical Values for the Simulated Reaction Systems

Parameter	Value	Unit
$\{\kappa_{i,0}\}$	[18 17 38 30]	M^{-1} h^{-1}
$\{E_i^*\}$	[150 200 350 400]	K

$$\begin{bmatrix} \dot{x}_1 \\ \hline \dot{x}_2 \end{bmatrix} = \begin{bmatrix} h(x_2)r(x) \\ \hline q_{\text{in}} \end{bmatrix}, \quad x_1(0) = \begin{bmatrix} -0.087 \\ -0.058 \\ -0.157 \end{bmatrix},$$
$$x_2(0) = \begin{bmatrix} -0.013 \\ 0.427 \end{bmatrix}, \quad (30)$$
$$c = (Kx_1 + C_{\text{in}}x_2 + Nx_3)/h(x_2),$$
$$V = h(x_2),$$

where

$$N = \begin{bmatrix} 0 & 0.008 & -0.362 & 0.370 & -0.724 & 0.450 & -0.072 \\ 0 & -0.071 & -0.166 & 0.095 & -0.332 & -0.639 & 0.663 \end{bmatrix}^T$$

and $x_3 = [0.025, -0.229]^T$. The time profiles of x_1 and x_2 are shown in Figure 3.

From $S_s = R = 3$ measurements, for example, $c_a = [c_A, c_D, c_G]^T$, the molar concentrations of the remaining species can be estimated using Eqs. 13 and 25 with

$$K_s = \begin{bmatrix} -1 & 0 & 0 \\ 1 & 1 & -1 \\ 0 & 0 & 1 \end{bmatrix}.$$

From Corollary 6 it can be seen that $p = 2$ inlet streams are not sufficient to have full state accessibility since at least (S

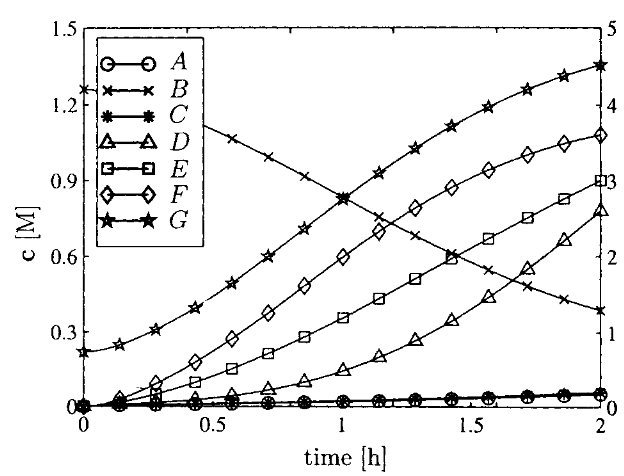

Figure 2. Time profiles of molar concentrations c.

Right axis for c_B and left axis for other species.

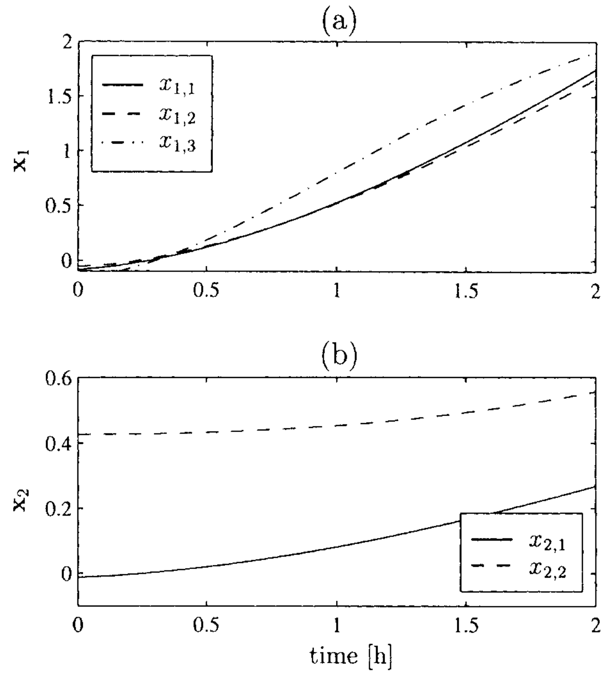

Figure 3. Time profiles of (a) x_1 and (b) x_2.

$-R) = 4$ inlet streams would be necessary. Furthermore, in the absence of an outlet stream ($q_{\text{out}} = 0$)—as is the case here—at least $p = R = 3$ inlet streams would be needed to guarantee feedback linearizability using Proposition 8.

Conclusions

A generic nonlinear transformation to normal form for reaction systems with inlet and outlet streams has been presented. It leads to a normal form where the reaction and flow invariants can be easily identified. Such a transformation was used to prove results on state accessibility. Implications of this transformation to normal form in the fields of model reduction, state reconstruction, and feedback linearizability were discussed. Using this transformation for feedback linearization has the advantage that the linearizing control can be obtained in a straightforward manner.

The results obtained for reaction systems with constant density, temperature, and inlet water concentrations were extended to varying density, nonisothermal and varying inlet concentration situations, and special cases such as semibatch reaction systems and CSTRs were considered. Note that the results obtained are *global* in nature and deal with the *full-fledged nonlinear* system, also for extensions and special cases. In summary, major insight is gained by using the normal form for reaction systems, which, in turn, can help to perform simulation, analysis, control, and optimization more efficiently.

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Appendix A: Proof of Theorem 2

The construction of the transformation to normal form was shown in the text. However, the reconstruction of the original states $\boldsymbol{n}$ and V from $\boldsymbol{x}$ and ν remains to be proven.

The relationship $\begin{bmatrix} \boldsymbol{n} \\ V \end{bmatrix} \to \begin{bmatrix} \boldsymbol{x} \\ \nu \end{bmatrix}$ is given in Eq. 8. The inverse can be obtained after a few algebraic manipulations as

$$\begin{bmatrix} z \\ V \end{bmatrix} = \begin{bmatrix} \boldsymbol{x}\nu \\ h(\boldsymbol{x}_2)\nu \end{bmatrix}. \tag{A1}$$

According to Eq. 6, the number of moles $\boldsymbol{n}$ satisfies

$$z = \begin{bmatrix} \boldsymbol{K}^+(\boldsymbol{I}_S - \boldsymbol{C}_{\text{in}}\boldsymbol{M}^T) \\ \boldsymbol{M}^T \\ \boldsymbol{N}^T \end{bmatrix}\boldsymbol{n}. \tag{A2}$$

Multiplying both sides of Eq. A2 by $[\boldsymbol{K}\ \boldsymbol{C}_{\text{in}}\ \boldsymbol{N}]$ and noting that $\boldsymbol{K}\boldsymbol{K}^+ + \boldsymbol{L}\boldsymbol{L}^T + \boldsymbol{N}\boldsymbol{N}^T = \boldsymbol{I}_S$,

$$\begin{aligned}[\boldsymbol{K}\boldsymbol{C}_{\text{in}}\ \boldsymbol{N}]z &= [\boldsymbol{K}\boldsymbol{K}^+(\boldsymbol{I}_S - \boldsymbol{C}_{\text{in}}\boldsymbol{M}^T) + \boldsymbol{C}_{\text{in}}\boldsymbol{M}^T + \boldsymbol{N}\boldsymbol{N}^T]\boldsymbol{n} \\ &= [\boldsymbol{K}\boldsymbol{K}^+ + (\boldsymbol{L}\boldsymbol{L}^T + \boldsymbol{N}\boldsymbol{N}^T)\boldsymbol{C}_{\text{in}}\boldsymbol{M}^T + \boldsymbol{N}\boldsymbol{N}^T]\boldsymbol{n} \\ &= (\boldsymbol{K}\boldsymbol{K}^+ + \boldsymbol{L}\boldsymbol{L}^T + \boldsymbol{N}\boldsymbol{N}^T)\boldsymbol{n} = \boldsymbol{n}. \end{aligned} \tag{A3}$$

Substituting $z = \boldsymbol{x}\nu$ into Eq. A3 leads to $\boldsymbol{n} = \nu(\boldsymbol{K}\boldsymbol{x}_1 + \boldsymbol{C}_{\text{in}}\boldsymbol{x}_2 + \boldsymbol{N}\boldsymbol{x}_3)$ and, hence, the theorem follows.

Appendix B: Proof of Corollary 3

The only difference between Corollary 3 and Theorem 2 is that $\boldsymbol{M} = \boldsymbol{L}(\boldsymbol{C}_{\text{in}}^T\boldsymbol{L})^+$. However, since $\boldsymbol{L}\boldsymbol{L}^T\boldsymbol{C}_{\text{in}}\boldsymbol{M}^T =$

$L(L^TC_{\text{in}})(L^TC_{\text{in}})^+L^T = LL^T$, the equation $KK^+ + LL^T + NN^T = I_S$ in the proof of Theorem 2 still holds and, hence, the corollary follows.

Appendix C: Proof of Proposition 7

Note that $c = n/V$. The measured and unmeasured molar concentrations induce the following partition in Eq. 12:

$$\frac{n}{\nu} = h(x_2)c = h(x_2)\begin{bmatrix} c_s \\ c_t \end{bmatrix} = \begin{bmatrix} K_s \\ K_t \end{bmatrix} x_1 + \begin{bmatrix} C_{\text{in},s} \\ C_{\text{in},t} \end{bmatrix} x_2 + \begin{bmatrix} N_s \\ N_t \end{bmatrix} x_3. \tag{C1}$$

The states x_2, x_3, and ν can be reconstructed from the inlet and outlet streams, c_0 and V_0, without knowledge of the kinetics. Owing to the existence of K_s^+, by assumption x_1 can be reconstructed from c_s as

$$x_1 = K_s^+[h(x_2)c_s - C_{\text{in},s}x_2 - N_s x_3]. \tag{C2}$$

Having reconstructed x_1, Eq. 13 follows.

Adding and subtracting the initial conditions of x_2 and noting that x_3 stay at their initial value, the estimate can be written as

$$\hat{c}_t = K_tK_s^+c_s + (C_{\text{in},t} - K_tK_s^+C_{\text{in},s})(\hat{x}_2 - \hat{x}_2(0))/\hat{h}$$
$$-(C_{\text{in},t} - K_tK_s^+C_{\text{in},s})\hat{x}_2(0)/\hat{h} + (N_t - K_tK_s^+N_s)\hat{x}_3(0)/\hat{h}. \tag{C3}$$

By assumption, there is no uncertainty in the initial volume, and material exchange terms. Using this fact and noting that $h_0\nu_0 = \hat{h}_0\hat{\nu}_0 = V_0$

$$\hat{\nu}\nu_0 = \nu\hat{\nu}_0, \qquad (x_2 - x_2(0))\nu_0 = (\hat{x}_2 - \hat{x}_2(0))\hat{\nu}_0, \qquad h\nu_0 = \hat{h}\hat{\nu}_0$$

and, thus,

$$(x_2 - x_2(0))/h = (\hat{x}_2 - \hat{x}_2(0))/\hat{h}. \tag{C4}$$

This means that there is no error in the estimation of $(x_2 - x_2(0))/h$. Using Eq. C4 and also the fact that c_s is measured without uncertainty, the estimation error $e \equiv \hat{c}_t - c_t$ becomes

$$e = \frac{-(C_{\text{in},t} - K_tK_s^+C_{\text{in},s})(\hat{x}_2(0)\nu_0/\hat{\nu}_0 - x_2(0)) + (N_t - K_tK_s^+N_s)(\hat{x}_3(0)\nu_0/\hat{\nu}_0 - x_3(0))}{h}. \tag{C5}$$

Note that the numerator in Eq. C5 is constant, which implies $d/dt(he) = 0_{S_t}$. Thus, the numerator is given by $e(0)h(x_2(0))$, leading to Eq. 14. The error dynamics are given by

$$\dot{e} = -de, \tag{C6}$$

where $d = (1_p^Tq_{\text{in}})/V$ is the so-called *dilution* term. If at least one of the inlet flow rates is nonzero for $t \to \infty$, then $d > 0$. Hence, the error dynamics (Eq. C4) are stable, and e converges asymptotically to 0_{S_t}. Consequently, the result proposed by Bastin and Dochain (1990) is obtained:

$$\lim_{t \to \infty} \hat{c}_t = c_t, \qquad d > 0. \tag{C7}$$

Appendix D: Proof of Proposition 8

A system is feedback linearizable if:

(FL1) the distributions $\Delta_i = \text{span}\{[f^kg_j]: 0 \le k \le i, 1 \le j \le m\}$ ($[\cdot,\cdot]$ denotes the Lie-bracket and $[f^kg_j]$ the iterated Lie-bracket $[f, f^{(k-1)}g_j]$) have constant rank everywhere and are closed under Lie-bracketing (involutive) for all $i \ge 0$, and

(FL2) rank $(\Delta_{n-1}) = n$.

Consider the distributions

$$\Delta_0 = \text{span}\{g_j, j = 1, \ldots, m\},$$
$$\Delta_1 = \text{span}\{g_j, [f, g_j], j = 1, \ldots, m\}. \tag{D1}$$

It can be verified that arranging the vectors of the distribution Δ_1 leads to

$$[g_1 \cdots g_m\,[f, g_1] \cdots [f, g_m]] = \begin{bmatrix} 0_{R\times m} & -J \\ I_m & 0_{m\times m} \end{bmatrix}. \tag{D2}$$

Since by assumption J is of rank R, it follows that rank $(\Delta_1) = (R + m)$, which is the maximum possible rank. Thus, Δ_1 is involutive. Furthermore, Δ_0 has rank m and is involutive since $[g_i, g_j] = 0$, $\forall i, j = 1, \ldots, p$, and $[g_i, g_m] = (g_m - g_i)/[\nu h(x_2)]$, $\forall i = 1, \ldots, m$. Thus, Eq. 14 is feedback linearizable.

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