Abstract—Reaction systems can be represented by first-principles models that describe the evolution of the states (typically concentrations, volume and temperature) by means of conservation equations of differential nature and constitutive equations of algebraic nature. The resulting models often contain redundant states since the various concentrations are not all linearly independent; indeed, the variability observed in the concentrations is caused by the reactions, the mass transferred between phases, the inlet and outlet streams. A minimal state representation is a dynamic model that exhibits the same behavior as the original model but has no redundant state. This paper considers the material balance equations associated with an open fluid–fluid reaction system that involves $S_i$ species, $R$ independent reactions, $p_i$ independent inlets and one outlet in the first fluid phase (e.g. the liquid phase) and $S_g$ species, $p_o$ independent inlets and one outlet in the second fluid phase (e.g. the gas phase). In addition, there are $p_m$ species transferring between the two phases. The $(S_l+S_g)$-dimensional model is transformed to $q = R + 2p_m + p_i + p_o + 2$ variant states and $S_l+S_g-q$ invariant states. Then, using the concept of accessibility of nonlinear systems, the conditions under which the transformed model is a minimal state representation are derived. It will be shown that the minimal number of concentration measurements needed to reconstruct the full state without kinetic information is $R + p_m$. The simulated chlorination of butanoic acid is used to illustrate the various concepts developed in the paper.

I. INTRODUCTION

First-principles models can include a large number of states, in particular when the system exhibits spatial variations and several time scales. However, some of the dynamic elements can be negligible or even redundant. Negligible states can be eliminated by introducing approximations. Reduction methods such as lumping, time-scale analysis and sensitivity analysis have been applied to the analysis of chemical reaction systems. In lumping, the state vector is reduced by combining similar variables [7]. Time-scale analysis exploits the difference in dynamics between fast and slow reactions. The fast reactions can be considered at quasi-steady state and the model order reduced by keeping the slow modes and eliminating the fast ones [14]. Sensitivity analysis examines the dynamical behavior of the reaction system with respect to parametric perturbations and identifies the important species and reactions to keep [8]. These reduction methods require information regarding the kinetics; furthermore, some information about species and reactions is lost in the reduced models.

In contrast, redundant states can be eliminated without introducing approximation nor using kinetic information. Redundant states are often present because the modeling step considers balance equations for more quantities than are necessary to represent the true variability of the process. For example, when modeling a closed homogeneous reaction system, one typically writes a mole balance equation for each of the $S$ species, whereas there are only $R < S$ reactions, that is $S - R$ equations are redundant. The situation is a bit more complicated in the open fluid–fluid reaction systems studied in this paper.

Process measurements are typically used for on-line monitoring, control and optimization of reaction systems. However, it is difficult to measure the concentrations of all the species due to limitations in the current state of sensor technology. Hence, it is necessary to reconstruct certain unmeasured concentrations from the available measurements. An important issue is then to assess the minimal number of concentration measurements that are needed to reconstruct the unmeasured states without kinetic information.

This paper considers open fluid–fluid (F–F) reaction systems. A transformation of the material balance equations is proposed to express the reaction system in terms of reaction variants, mass-transfer variants, inlet-flow variants, outlet-flow variant and invariants. Using the concept of accessibility of nonlinear systems, the conditions under which the transformed model is a minimal state representation are investigated. Then, using the state transformation, one can determine the minimal number of measured concentrations that are necessary to reconstruct the concentration of all species.

The paper is organized as follows. Section II introduces the model of open F–F reaction systems as well as several definitions. In Section III, a nonlinear transformation of the numbers of moles to various variant and invariant states is proposed. The conditions for minimal state representation of the transformed model are derived in Section IV. Section V proposes an approach to reconstruct the unmeasured concentrations in F–F reaction systems. The theoretical developments are illustrated through a simulation example in Section VI, and Section VII concludes the paper.

II. PRELIMINARY

A. Model of open fluid–fluid reaction systems

The mole balance equations for a fluid–fluid reaction system are presented in this section. A fluid–fluid reaction system consists of two phases, namely, the G and L phases.
The two phases are modeled separately, with the mass-transfer rates ζ connecting the two. The G phase contains \(S_g\) species, \(p_g\) inlets and one outlet, while the L phase contains \(S_l\) species, \(p_l\) inlets and one outlet. There are \(p_m\) mass transfers taking place between the two phases.

With the assumptions:

(A1) The G and L phases are homogeneous,

(A2) the reactions take place in the bulk of the L phase only,

(A3) mass transfer rates are considered positive from the G phase to the L phase,

(A4) the mass-transfer phenomena are described by the two-film theory with no accumulation in the boundary layer,

the mole balances for the G and L phases are:

\[
\dot{n}_g(t) = W_{in,g} u_{in,g}(t) - W_{m,g} \zeta(t) - \frac{u_{out,g}(t)}{m_g(t)} n_g(t), \quad n_g(0) = n_{g0}, \tag{1}
\]

and

\[
\dot{n}_l(t) = N^T V_l(t) r(t) + W_{in,l} u_{in,l}(t) + W_{m,l} \zeta(t) - \frac{u_{out,l}(t)}{m_l(t)} n_l(t), \quad n_l(0) = n_{l0}, \tag{2}
\]

where \(n_f\) is the \(S_f\)-dimensional vector of the numbers of moles in the \(f\) phase, \(f \in \{g, l\}\). \(N\) the \((R \times S_i)\)-dimensional stoichiometric matrix. \(R\) the number of reactions, \(W_{in,f} = M_{w,f}^{-1} W_{in,f}\) the \((S_f \times p_f)\)-dimensional inlet matrix expressing the inlet concentrations to the \(f\) phase, \(M_{w,f}\) the \(S_f\)-dimensional diagonal matrix of molecular weights, and \(W_{in,f} = [\hat{w}_{in,f}^1 \cdots \hat{w}_{in,f}^{p_f}]\) with \(\hat{w}_{in,f}^k\) being the \(S_f\)-dimensional vector of weight fractions of the \(k\)th inlet to the \(f\) phase, \(u_{in,f}\) the \(p_f\)-dimensional inlet mass flow rate to the \(f\) phase, and \(n_{f0}\) the vector of initial moles in the \(f\) phase. \(\zeta\) is the \(p_m\)-dimensional vector of mass-transfer rates, \(W_{m,f} = M_{w,f}^{-1} \bar{E}_{m,f}\) is the \((S_f \times p_m)\)-dimensional mass-transfer matrix to the \(f\) phase, \(\bar{E}_{m,f} = [\hat{e}_{m,f}^1 \cdots \hat{e}_{m,f}^{p_m}]\) with \(\hat{e}_{m,f}^k\) being the \(S_f\)-dimensional vector with the element corresponding to the \(k\)th transferring species equal to unity and the other elements equal to zero. Note that the mass of each phase can be inferred from the numbers of moles as:

\[
m_f(t) = 1_{S_f}^{T} M_{w,f} n_f(t), \quad f \in \{g, l\}. \tag{3}
\]

Throughout this paper, the \(R\) reactions, the \(p_m\) mass transfers and the \(p_f\) inlets are assumed to be independent, according to the definitions given in Amrhein et al. [1] and Bhatt et al. [3].

### B. Minimal state representation

A minimal state representation contains the minimal number of state variables, while exhibiting identical dynamic behavior as the original representation. This section introduces the mathematical definitions of minimal state representation and local state accessibility.

---

**Definition 1 (Minimal state representation)**

Consider the following class of input-affine nonlinear systems:

\[
w(t) = f(w(t)) + \sum_{i=1}^{p} g_i(w(t))u_i(t), \quad w(0) = w_0, \tag{4}
\]

where \(w \in \mathbb{R}^n\) is the state vector and \(u \in \mathbb{R}^p\) the input vector. It will be assumed that \(f : \mathbb{R}^n \to \mathbb{R}^n\) and \(g_i : \mathbb{R}^n \to \mathbb{R}^n\) are Lipschitz with respect to \(w\).

Consider the following two conditions:

1. (Representation condition):

   \[
   \begin{align*}
   &\text{The transformation } \Phi : \mathbb{R}^n \to \mathbb{R}^n, \text{ independent of the inputs } u, \\
   &\xi = \Phi(w), \quad \xi \in \mathbb{R}^n, \quad \xi = [\xi_1^T \quad \xi_2^T]^T, \\
   &\text{transforms } (4) \text{ to:} \\
   &\begin{cases}
   \dot{\xi}_1 = f(\xi) + \sum_{i=1}^{p} g_i(\xi)u_i, \\
   \dot{\xi}_2 = 0_{n-q},
   \end{cases} \tag{5}
   \end{align*}
   \]

   \[
   \xi_1(0) = \xi_{1,0}, \quad \xi_2(0) = \xi_{2,0}. \tag{6}
   \]

   \[
   \sum_q : \xi_1 \in \mathbb{R}^q, \quad \xi_2 \in \mathbb{R}^{n-q}, \tag{7}
   \]

   \[
   f : \mathbb{R}^n \to \mathbb{R}^q, \quad \tilde{g} : \mathbb{R}^n \to \mathbb{R}^q, \text{ with } q \leq n.
   \]

   \[
   \text{The back transformation } \Phi^{-1} : \mathbb{R}^n \to \mathbb{R}^n, \text{ independent of the inputs } u, \\
   \mathbf{w} = \Phi^{-1}(\xi), \tag{8}
   \]

   \[
   \text{transforms } (6) \text{ and } (7) \text{ back to } (4).
   \]

2. (Minimality condition): There does not exist a positive integer \(l < q\) such that \(\Sigma_l\) holds.

   If there exists a positive integer \(q\) that satisfies the representation and minimality conditions, then (6) is a minimal state representation of (4) and \(q\) is the corresponding minimal order.

To satisfy the representation condition, one needs to construct the transformation \(\Phi\) such that the original states \(\mathbf{w}\) are transformed into the \(q\) variant states \(\xi_1\) and the \(n-q\) invariant states \(\xi_2\) that are not controllable.

To check that \(\xi_1\) satisfies the minimality condition, the concept of minimal realization of nonlinear systems can be used [10], [11], [12], [5]. For linear systems, it is well known that minimal realizations are both observable and controllable [9]. The concept of observability of linear systems can easily be extended to nonlinear systems. For example, the observability of a realization can be checked by regrouping — into equivalence classes — indistinguishable system trajectories that obey a given input-output relationship. In this manner, the resulting equivalence classes are observable, thereby leading to an observable realization (observable quotient system) [12]. In contrast to observability, there is no simple extension to nonlinear systems of the concept of controllability of linear systems [13]. In [11] and [13], the concept of state accessibility has been introduced, which is related to controllability. In [11], the concept of accessibility has been used to give sufficient conditions for the minimality of a given state-space realization. Similarly, in [10], sufficient
conditions in terms of controllability and observability functions for a given state-space realization to be minimal have been developed using a nonlinear extension of the Gramians. Furthermore, an algorithm has been proposed to construct a basis of exact one-forms, from which the minimal realization can be obtained [5]. In this paper, minimality according to Definition 1 is based on the concept of state accessibility as described in [11], which is briefly reviewed next.

Consider the class of input-affine nonlinear dynamical systems defined in (4). A system is locally state accessible if, for every initial state \( w_0 \), the set of states reachable from \( w_0 \) has a nonempty interior. Mathematically, this can be expressed by the following definition [13].

**Definition 2 (Local state accessibility)**

Let \( U: [0, T] \rightarrow \mathbb{R}^p \) denote the set of vector-valued input functions and \( W(w_0, U, t) \) the solution at time \( t \) starting from the initial condition \( w_0 \in \mathbb{R}^n \). The system (4) is locally state accessible from \( w_0 \) if there exists an open neighborhood \( O \subseteq \mathbb{R}^n \) for which \( W(w_0, U, T) \in O \).

Let us define the accessibility distribution as the span of the Lie algebra that contains the set of vector fields \( f, g_1, g_2, \ldots, g_p \), and all the repeated Lie brackets of vector fields generated by \( f \) and \( g_i \). More precisely, given the integer \( k \), define \( \Delta_k \) as:

\[
\Delta_k = \text{span}(Y_1, Y_2, \ldots, Y_k),
\]

where \( Y_j, 1 \leq j \leq s \), are all possible expressions

\[
[x_i, [x_{i-1}, \ldots, x_2, x_1], \ldots], \quad 1 \leq l \leq k,
\]

where each \( x_i \) can be any vector field (repeated vector fields are allowed) in the set \( \{f, g_1, g_2, \ldots, g_p\} \). The \( \Delta_k \) induce a nested set of distributions, \( \Delta_1 \subset \Delta_2 \subset \cdots \subset \Delta_k \), which converges for \( k = \bar{k} \) in the sense that \( \dim(\Delta_{k+1}) = \dim(\Delta_k) \). Let us denote \( \Delta_k \) by \( \tilde{\Delta} \). The local state accessibility of input-affine nonlinear dynamical systems from a given state \( w_0 \) is given by the following lemma.

**Lemma 1 ([13], [2])**

If \( \dim(\tilde{\Delta}(w_0)) = n \) at \( w_0 \in \mathbb{R}^n \), then the system (4) is locally state accessible from \( w_0 \).

If the condition in the lemma holds for every \( w_0 \), then the system is said to be locally state accessible.

**Lemma 2**

If the system (6) is locally state accessible, its state dimension cannot be reduced.

**Proof:** First note that the system (6) is of dimension \( q \) as the "states" \( \xi_2, \xi_3 \) can be considered as constant parameters with values \( \xi_{2,0}, \xi_{3,0} \). The proof of Lemma 2 follows by contradiction. Let us assume that there exists a transformation \( \Phi: \xi_2 \rightarrow y = [y_1^T, y_2] \) independent of the inputs such that the dynamics of the system (6) can be reduced as follows:

\[
\begin{align*}
\dot{y}_1 &= f(y) + \sum_{i=1}^p g_i(y)u_i, \\
\dot{y}_2 &= 0.
\end{align*}
\]

The states \( y_2 \) are inaccessible since they are not affected by the inputs. However, since the system (6) is assumed to be locally accessible, there cannot exist such a transformation. It follows that the dimension of the states \( \xi \) cannot be reduced.

### III. Nonlinear Transformation of the States \( n_i(t) \) and \( n_g(t) \)

The aim of this section is to propose a one-to-one nonlinear transformation of the numbers of moles in the G and L phases to reaction variants, mass-transfer variants, inlet-flow variants, outlet-flow variant, and invariants. The nonlinear transformation will be developed separately for \( n_i(t) \) and \( n_g(t) \).

#### A. Five-way decomposition of \( n_i(t) \)

**Theorem 1 (Nonlinear transformation of \( n_i(t) \))**

Consider the \( L \) phase of the \( F \)–reaction system given by (2).

If \( \text{rank}([N^T \ W_{m,l} W_{m,l}]) = R + p_m + p_l \), there exists a diffeomorphism \( \Psi:[n_i] \rightarrow [\xi] \) such that:

\[
[n_i] \rightarrow [\xi]^{T} \begin{bmatrix}
\xi_x, \\
\xi_{m,i}, \\
\xi_{r,i}, \\
\lambda_l
\end{bmatrix} = \begin{bmatrix}
S^T n_i \\
M^T_{m,i} n_i \\
M^T_{r,i} n_i \\
Q^T_{r,i,j} n_i / g_i(n_i)
\end{bmatrix},
\]

with

\[
g_i(n_i) = \begin{cases}
q_i^T n_i & \text{if } q_i^T n_i \neq 0, \\
\eta_l & \text{if } q_i^T n_i = 0,
\end{cases}
\]

\[
S^T = N^T + (I_{S_l} - W_{m,l} M^T_{m,l} - W_{m,l} M^T_{r,l}), \quad \text{and } \eta_l \text{ a non-zero arbitrary real constant.}
\]

The diffeomorphism transforms \( n_i \) to the reaction variants \( x_r \), the mass-transfer variants \( x_{m,i} \), the inlet variants \( x_{in,l} \), the outlet flow variant \( \lambda_l \), and the invariants \( x_{r,i/l} \). The transformed state equations read:

\[
\begin{align*}
\dot{x}_r &= \psi^{i} \psi_{r} - \frac{u_{out,l}}{m_l} x_r, \\
x_{m,i} &= \psi^{i} \psi_{m,i} - \frac{u_{out,l}}{m_l} x_{m,i}, \\
x_{in,l} &= \frac{u_{in,l}}{m_l} x_{in,l} - \frac{u_{out,l}}{m_l} x_{m,i}, \\
x_{r,i/l} &= \psi^{i} \psi_{r,i} - \frac{u_{out,l}}{m_l} x_{r,i/l}, \\
\lambda_l &= -(u_{out,l}/m_l) \lambda_l, \\
\lambda_l &= g_i(n_i),
\end{align*}
\]

where \( M_{m,i} \) is the \( (S_l \times p_m) \)-dimensional matrix corresponding to the first \( p_m \) columns of \( M_l \) and \( M_{r,i/l} \) is the \( (S_l \times p_l) \)-dimensional matrix corresponding to the last \( p_l \) columns of \( M_l \). Without loss of generality, \( q_i \) is a \( S_l \)-dimensional vector corresponding to an arbitrary column of \( Q_{r,i/l} \). \( V_{r,i,l} \) is a \( (S_l \times (S_l - R - p_m - p_l - 1)) \)-dimensional matrix corresponding to the remaining columns of \( Q_l \). The matrices \( S_l \), \( M_l \) and \( Q_l \) are computed using the algorithm given in Appendix A of [1]. The back transformation \( \Psi^{-1}_l: [\xi] \rightarrow n_i \) enables the reconstruction of the numbers of moles \( n_i(t) \) from the states \( x_i(t) \) and \( \lambda_l(t) \) as follows:

\[
\begin{align*}
n_i(t) &= N^T x_i(t) + W_{m,l} x_{m,i}(t) \\
&+ W_{m,l} x_{m,i}(t) + h_l \lambda_l(t),
\end{align*}
\]
with
\[ h_t = Q^1 \left[ x_{m,g} \right] . \]  

(Proof follows from Theorem 2 in [4])

B. Four-way decomposition of \( n_g(t) \)

Corollary 1 (Nonlinear transformation of \( n_g(t) \))

Consider the \( G \) phase of the F-F reaction system given by (1). If \( \text{rank} \left( \left[ W_{m,g} \ W_{m,g} \right] \right) = p_m + p_g \), there exists a diffeomorphism \( \Psi_g: [n_g] \to \left[ x_g \right] \) such that:

\[ [n_g] \to \left[ x_g \right] : \begin{bmatrix} x_{m,g} \\ x_{v,g} \\ \lambda_g \end{bmatrix} = \begin{bmatrix} M^T_{m,g} n_g \\ M^T_{v,g} n_g \\ Q^T_{v,g} n_g / g_g(n_g) \end{bmatrix} \]

with
\[ g_g(n_g) = \left\{ \begin{array}{ll} q^T_g n_g & \forall q^T_g n_g \neq 0, \\ \eta_g & \forall q^T_g n_g = 0, \end{array} \right. \]

and \( \eta_g \) a non-zero arbitrary real constant. The diffeomorphism transforms \( n_g \) to the mass-transfer variants \( x_{m,g} \), the inlet variants \( x_{v,g} \), the outlet variant \( \lambda_g \), and the invariants \( x_{v,g} \). The transformed states read:

\[ \dot{x}_{m,g} = \zeta \frac{m_{out,g}}{m_g} x_{m,g}, \quad x_{m,g}(0) = M^T_{m,g} n_g, \]
\[ \dot{x}_{v,g} = u_{v,g} - \frac{m_{out,g}}{m_g} x_{v,g}, \quad x_{v,g}(0) = M^T_{v,g} n_g, \]
\[ \dot{\lambda}_g = -\left( u_{m,g}/m_g \right) \lambda_g, \quad \lambda_g(0) = g_g(n_g), \]

where \( M_{m,g} \) is the \((S_g \times p_m)\)-dimensional matrix corresponding to the first \( p_m \) columns of \( M_g \) and \( M_{v,g} \) is the \((S_l \times p_g)\)-dimensional matrix corresponding to the last \( p_g \) columns of \( M_g \). Without loss of generality, \( q_g \) is a \( S_g \)-dimensional vector corresponding to an arbitrary column of \( Q_g \); \( Q_{v,g} \) is \([(S_g \times p_g) - p_g - 1] \)-dimensional matrix corresponding to the remaining columns of \( Q_g \). The matrices \( M_g \) and \( Q_g \) are computed using the algorithm given in Appendix A of [1]. The back transformation \( \Psi_g^{-1}: \left[ x_g \right] \to [n_g] \) enables the reconstruction of the numbers of moles \( n_g(t) \) from the states \( x_g(t) \) and \( \lambda_g(t) \) as follows:

\[ n_g(t) = -W_{m,g} x_{m,g}(t) + W_{m,g} x_{i,g}(t) + h_g \lambda_g(t) \]

with
\[ h_g = Q_g \left[ x_{v,g} \right] . \]

(Proof follows from Theorem 2 in [4])

C. Alternative model

The diffeomorphisms \( \Psi_t \) and \( \Psi_g \) lead to the transformed model given by (15) and (21). To simplify the representation, an alternative model can be generated as follows. Let us introduce the \( p_m \)-dimensional vector

\[ \delta_m(t) := x_{m,g}(t) - x_{m,l}(t) \]

that expresses the differences in mass-transfer variants between the \( G \) and \( L \) phases. The dynamic equation for \( \delta_m \) can be expressed independently of \( \zeta \):

\[ \delta_m = -\frac{m_{out,l}}{m_l} \delta_m + \left( \frac{m_{out,l}}{m_l} - \frac{m_{out,g}}{m_g} \right) x_{m,g}, \]

\[ \delta_m(0) = M^T_{m,g} n_{g0} - M^T_{m,l} n_{l0}. \]

This way, the mass-transfer variants can be expressed with only \( p_m \) differential equations involving the unknown mass-transfer rates \( \zeta \). With \( \delta_m \) used to express \( x_{m,i} \) from \( x_{m,g} \), the transformed model given by (15) and (21) can be put in the form of (6) with the state vectors \( \xi_1 = [x_{v,l}^T \ x_{v,g}^T \ \delta_m^T \ x_{i,l}^T \ x_{i,g}^T \ \lambda_l \ \lambda_g] \) and \( \xi_2 = [x_{v,l}^T \ x_{v,g}^T] \) \( q^T = R + 2p_m + p_l + p_g + 2 \) and \( S_I + S_G + 2 \), respectively:

\[ \dot{\xi}_1 = f(\xi) + \sum_{i=1}^{p} g_i(\xi) u_i, \quad \xi_1(0) = \xi_{1,0}, \]

\[ \dot{\xi}_2 = 0_{n-q}, \quad \xi_2(0) = \xi_{2,0}, \]

with
\[ \dot{f} = \left[ f_1(\xi)^T \right], \quad \dot{g}_1 = \left[ g_{1,p} \right], \quad \dot{g}_p = \left[ g_{p+1} \right], \quad \xi_{1,0} = \left[ \xi_{1,0} \right] \]

and \( \text{u} = \left[ u_{m,l}^T \right. \ u_{v,l}^T \ \lambda_l \ \lambda_g]^T \),

where \( u \) is the \( p \)-dimensional input vector, with \( p = p_l + p_g + 2 \), and \( \dot{f}, f, \) and \( \zeta \) are \( q^T, R^T \) and \( p_m \)-dimensional vector fields, respectively.

IV. MINIMAL STATE REPRESENTATION

This section will investigate the minimal state property of the transformed model (26), namely the representation and minimality conditions.

A. Representation condition

The transformations from \( [n_1^T \ n_2^T] \) to \( [\xi_1^T \ \xi_2^T] \) encompass the diffeomorphisms \( \Psi_t \) and \( \Psi_g \) and the substitution of \( \dot{x}_{m,i} \) by \( \delta_m \), which is invertible. Hence, the representation condition of Definition 1 is fulfilled.

B. Minimality condition

If the two phases are treated separately, the model involves \( 2p_m \) mass-transfer variants, namely \( p_m \) for each phase. Since there are only \( p_m \) mass transfers in the system, the question arises as to whether it is possible to reduce the number of mass-transfer variants from \( 2p_m \) to \( p_m \) when the \( G \) and \( L \) phases are treated simultaneously. It will be shown next that such a reduction in the number of mass-transfer variants is not possible.

\[ 1 \]Without this substitution, both \( x_{m,g} \) and \( x_{m,l} \) would have been functions of \( \zeta \).
Theorem 2 (Dimensionality of mass transfer)
Consider the mass-transfer subsystems of the transformed model system given by (15) and (21):
\[
\begin{align*}
\dot{x}_{m,l} &= \zeta - \left(\frac{u_{out,l}}{m_l}\right)x_{m,l}, \quad x_{m,l}(0) = M_{m,l}^* n_{l0}, \\
\dot{\lambda}_l &= -\left(\frac{u_{out,l}}{m_l}\right)\lambda_l, \quad \lambda_l(0) = g_l(n_{l0}), \\
\dot{x}_{m,g} &= \zeta - \left(\frac{u_{out,g}}{m_g}\right)x_{m,g}, \quad x_{m,g}(0) = M_{m,g}^* n_{g0}, \\
\dot{\lambda}_g &= -\left(\frac{u_{out,g}}{m_g}\right)\lambda_g, \quad \lambda_g(0) = g_g(n_{g0}).
\end{align*}
\] (27)
Then, except for some pathological case, if \(\lambda_l \neq 0\) and \(\lambda_g \neq 0\), the dimension of the system (27) cannot be reduced.

**Proof:** First, note that, if \(u_{out,g}(t) = \frac{u_{out,g}(t)}{m_g(t)}x_{m,g}(t) = x_{m,g}(t)\) and \(\lambda_l(t) = \lambda_l(t)\), the number of states in system (27) reduces from \(2m + 2\) to the \(m + 1\) states \(x_{m,l}\) and \(\lambda_l\) in (27). This case is pathological and rare in practice.

Upon defining \(y_1 := x_{m,l}, y_2 := \lambda_l, y_3 := x_{m,g}, y_4 := \lambda_g, u_1 := \zeta, u_2 := -\frac{u_{out,l}}{m_l}1\) and \(u_3 := -\frac{u_{out,g}}{m_g}\), the system (27) can be written as:
\[
\begin{bmatrix}
\dot{y}_1 \\
\dot{y}_2 \\
\dot{y}_3 \\
\dot{y}_4
\end{bmatrix} = G_1 u_1 + g_2 u_2 + g_3 u_3,
\] (28)
with
\[
G_1 = \begin{bmatrix}
I_{p_m \times p_m} & 0_{p_m \times p_m} & 0_{p_m \times p_m} \\
0_{1 \times p_m} & I_{p_m \times p_m} & 0_{p_m \times p_m} \\
0_{1 \times p_m} & 0_{p_m \times p_m} & I_{p_m \times p_m}
\end{bmatrix},
\] (29)
Let \(\Delta\) be the converged accessibility distribution of (28):
\[
\Delta = \text{span}\{G_1, g_2, \ldots, [G_1, g_2], [G_1, g_3], \ldots\}
\]
\[
\begin{bmatrix}
I_{p_m \times p_m} & -y_1 & 0_{p_m} & 0_{p_m} \\
0_{1 \times p_m} & -y_2 & 0_{p_m} & 0_{p_m} \\
0_{1 \times p_m} & 0_{p_m} & -y_3 & 0_{p_m} \\
0_{1 \times p_m} & 0_{p_m} & 0_{p_m} & -y_4
\end{bmatrix}.
\] (30)
It follows that, for \(y_2 \neq 0\) and \(y_4 \neq 0\), \(\Delta\) has full rank \(2m + 2\). Hence, the system (27) is locally state accessible and, according to Lemma 2, its state dimension cannot be reduced.

Next, the conditions under which (26) is a minimal state representation of the open F–F reaction system (1)-(2) are given in the following theorem.

Theorem 3 (Minimal state representation)
Consider the F–F reaction system (1)-(2) and the transformed system (26). If (i) \(\text{rank}(\begin{bmatrix} N^T & W_{m,l} & W_{m,g} \end{bmatrix}) = R + p_m + p_l\) and (ii) \(\text{rank}(\begin{bmatrix} W_{m,g} & W_{m,g} \end{bmatrix}) = p_m + p_g\), then the system (26) is a minimal state representation of the system (1)-(2).

**Proof:** Conditions (i) and (ii) ensure that the diffeomorphisms \(\Psi_1\) and \(\Psi_g\) exist. The transformed model (26) contains decoupled differential equations for \(x_r, x_{n,l}\) and \(x_{n,g}\), which are accessible independently via \(r, u_{n,l}\) and \(u_{n,g}\), respectively. The other differential equations for \(x_{m,l}\), \(x_{m,g}\), \(\lambda_l\) and \(\lambda_g\) have been shown in Theorem 2 to be locally accessible from \(\zeta, u_{out,l}/m_l\) and \(u_{out,g}/m_g\). Hence, the system is locally state accessible from the inputs \(r, u_{n,l}, u_{n,g}, \zeta, u_{out,l}/m_l\) and \(u_{out,g}/m_g\). It follows from Lemma 2 that the transformed system (26) is a minimal state representation of the system (1)-(2). The minimal order is \(q = R + 2p_m + p_l + p_g + 2\).

V. STATE RECONSTRUCTION

An approach for reconstructing the unmeasured concentrations in the G and L phases using selected concentration and flow rate measurements, but without kinetic information, is developed next for open F–F reaction systems. It will be shown that the minimal number of concentration measurements needed to reconstruct the full state is \(R + p_m - 2\).

Let \(n_{l,u}(t)\) and \(n_{g,u}(t)\) be the \(S_{l,u}\) and \(S_{g,u}\)-dimensional vectors of the available numbers of moles in the L and G phases, respectively. In addition, the inlet and outlet flow rates \(u_{m,l}, u_{m,g}, u_{out,l}\) and \(u_{out,g}\) are also measured. The matrices \(N, W_{m,l}, W_{m,g}, W_{l,m,l}, W_{in,g}\) and \(W_{in,l}\) and the initial conditions \(n_{l0}\) and \(n_{g0}\) are known. The corresponding quantities associated with the available species are noted \(N_{m,l}, W_{m,l,a}, W_{m,g,a}, W_{l,m,l,a}, W_{in,g,a}, n_{l0,a}\) and \(n_{g0,a}\). Similarly, for the unmeasured species, we have \(N_{u}, W_{m,l,u}, W_{m,g,u}, W_{l,m,l,u}, W_{in,g,u}, n_{l0,u}\) and \(n_{g0,u}\). The objective of this section is to (i) reconstruct the unmeasured numbers of moles \(n_{l,u}(t)\) in the L phase and \(n_{g,u}(t)\) in the G phase, and (ii) compute the profiles of the variant states \(x_r, x_{n,l}, x_{n,g}, x_{m,l}, x_{m,g}, \lambda_l\) and \(\lambda_g\) without knowledge of reaction and mass-transfer rates.

The number of state variables in the transformed system (26) is \(q = R + 2p_m + p_l + p_g + 2\). There are corresponding differential equations for \(x_r, x_{n,l}, x_{n,g}, \delta_m, x_{m,l}, x_{m,g}, \lambda_l\) and \(\lambda_g\) given by (15), (21) and (25). The unknown quantities in these equations are \(r, \zeta, m_l\) and \(m_g\). The masses \(m_l\) and \(m_g\) can be calculated from the various variants as follows:
\[
m_l(t) = I_{p_m} x_{m,l}(t) + I_{p_l} x_{m,l}(t) + I_{p_g} M_{w,g} h_2 \lambda_l(t),
\]
\[
m_g(t) = I_{p_m} x_{m,g}(t) + I_{p_l} x_{m,g}(t) + I_{p_g} M_{w,g} h_g \lambda_g(t).
\] (31)
Hence, there remain only the \(R + p_m\) unknown quantities \(r\) and \(\zeta\), for the determination of which at least \(R + p_m\) “appropriate” measurements are necessary. The wording “appropriate” is important here as not any \(R + p_m\) measurements will do. A certain difficulty results from the fact that the mass-transfer variants can be computed from information stemming from either phase.

Let us consider the case with \(p_{m,y}\) mass-transfer variants computed from the G phase and \(p_{m,l} = p_m - p_{m,y}\) mass-transfer variants computed from the L phase. The mass-transfer variants and the mass-transfer matrices are noted accordingly. For instance, \(x_{m,y}\) and \(x_{m,g}\) represent the \(p_{m,y}\)-dimensional vectors of mass-transfer variants computed from the G phase measurements for the L and G phases, respectively; \(x_{m,l}\) is the \(p_{m,l}\)-dimensional vector of mass-transfer

\[V_l(t) c_l(t)\]
variants computed from and for the L phase; \( W_{m_l,t,a} \) is the \( (S_{l,a} \times p_m) \)-dimensional mass-transfer matrix associated with the \( p_m \) mass transfers and the \( S_{l,a} \) species; \( W_{m_g,t,a} \) is the \( (S_{l,a} \times p_m) \)-dimensional mass-transfer matrix associated with the \( p_m \) mass transfers and the \( S_{l,a} \) species; \( W_{m_g,g,a} \) is the \( (S_{g,a} \times p_m) \)-dimensional mass-transfer matrix associated with the \( p_m \) mass transfers and the \( S_{g,a} \) species.

The measured numbers of moles are related to the various variants as follows:

\[
\begin{align*}
\mathbf{n}_{l,a}(t) &= N_{l,a}^T \mathbf{x}(t) + W_{m_l,t,a} \mathbf{x}_{m_l,t}(t) + W_{m_l,g,a} \mathbf{x}_{m_l,g}(t) \\
&+ W_{in,l,a} \mathbf{x}_{in,l}(t) + h_{l,a} \mathbf{x}_{l}(t), \\
\mathbf{n}_{g,a}(t) &= -W_{m_g,g,a} \mathbf{x}_{m_g,g}(t) - W_{m_1,g,a} \mathbf{x}_{m_1,g}(t) \\
&+ W_{in,g,a} \mathbf{x}_{in,g}(t) + h_{g,a} \mathbf{x}_{g}(t).
\end{align*}
\]

(32)

The following theorem specifies the conditions that the measurements have to satisfy to be able to reconstruct the unmeasured numbers of moles without kinetic information.

**Theorem 4 (Minimal number of measurements)**

Let the matrices \( N_l \), \( W_{m_l,t,a} \), \( W_{m_g,t,a} \), \( W_{m_g,g,a} \), and the initial conditions \( n_{0l} \) and \( n_{0g} \) be known. The quantities \( n_{l,a}(t) \), \( n_{g,a}(t) \), \( u_{in,l,t}(t) \), \( u_{in,g,t}(t) \), and \( u_{out,g,t} \) are assumed to be measured. If (i) \( S_{l,a} + S_{g,a} \geq R + p_m \), (ii) \( \text{rank}(N_{l,a}^T W_{m_l,t,a}) = R + p_{m_l} \), and (iii) \( \text{rank}(W_{m_g,g,a}) = p_m \), then the unknown quantities \( r \) and \( \zeta \) can be reconstructed and with them the variants \( x_l(t) \), \( x_{m_l,g}(t) \), \( x_{m_l,g}(t) \), \( x_{l}(t) \), \( x_{m_l,g}(t) \), \( x_{m_l,g}(t) \), \( \lambda_{l}(t) \), and \( \lambda_{g}(t) \).

With the knowledge of the initial conditions \( n_{l,a}(t) \) and \( n_{g,a}(t) \) of the unmeasured species, the corresponding unmeasured numbers of moles \( n_{l,a}(t) \) and \( n_{g,a}(t) \) can be reconstructed from the computed variants as follows:

\[
\begin{align*}
\mathbf{n}_{l,a}(t) &= N_{l,a}^T \mathbf{x}(t) + W_{m_l,t,a} \mathbf{x}_{m_l,t}(t) + W_{in,l,a} \mathbf{x}_{in,l}(t) \\
&+ h_{l,a} \mathbf{x}_{l}(t), \\
\mathbf{n}_{g,a}(t) &= -W_{m_g,g,a} \mathbf{x}_{m_g,g}(t) + W_{in,g,a} \mathbf{x}_{in,g}(t) + h_{g,a} \mathbf{x}_{g}(t).
\end{align*}
\]

(33)

**Proof:** Since \( \text{rank}(N_{l,a}^T W_{m_l,t,a}) \geq R + p_{m_l} \), there are at least \( R + p_{m_l} \) independent algebraic equations out of the \( S_{l,a} \) equations for the L phase. Similarly, it follows from \( \text{rank}(W_{m_g,g,a}) = p_g \) that there are at least \( p_g \) independent algebraic equations out of the \( S_{g,a} \) equations for the G phase. Since \( p_{m_l} + p_{m_l} = p_m \) by construction, the number of independent equations is equal to the number of unknown variables. Hence, the measurements provide the information necessary to reconstruct the unknown quantities \( r \) and \( \zeta \) and with them the variants \( x_l(t) \), \( x_{m_l,g}(t) \), \( x_{m_l,g}(t) \), \( x_{l}(t) \), \( x_{m_l,g}(t) \), \( \lambda_{l}(t) \), and \( \lambda_{g}(t) \) Then, the computed variables can be used to reconstruct \( n_{l,a}(t) \) and \( n_{g,a}(t) \) using (33). This proves the theorem.

In addition to at least \( R + p_m \) concentration measurements, the \( p_l + p_g \) inlet flow rates and two outlet flow rates need to be measured. Hence, the minimal number of measurements to compute all the variants is \( R + p_m + p_g + p_l + 2 \). On the other hand, it follows from Theorem 3 that the minimal number of states is \( R + 2p_m + p_g + p_l + 2 \). These results are not contradictory because, in addition to the \( R + p_m + p_g + p_l + 2 \) measurements, the \( p_m \) differential equations describing the states \( \delta_m \) are needed to reconstruct the unmeasured states.

**VI. Simulation Study**

The chlorination of butanoic acid (a gas-liquid reaction system) described in [3] is considered to illustrate the concept of state reconstruction. Butanoic acid (BA) reacts with \( \text{Cl}_2 \) to produce MBA, DBA, and HCl via two parallel reactions. The reactions take place in the liquid phase, with \( \text{Cl}_2 \) transferring from the gas to the liquid and HCl from the liquid to the gas. The reaction system is simulated for 1.5 h, and it is assumed that noisy measurements (additive zero-mean Gaussian noise) are available every 54 s. The numbers of moles of air, \( \text{Cl}_2 \) and HCl are measured in the gas phase (\( S_{g,a} = 3 \), standard deviation \( \sigma_g = 0.003 \) kmol, see Figure 1) and the numbers of moles of BA and MBA are available in the liquid phase (\( S_{l,a} = 2 \), \( \sigma_l = 0.02 \) kmol, see Figure 2). The liquid phase has no inlet and no outlet. The inlet gas flow rate \( u_{in,g} \) is adjusted to control the pressure in the reactor. The gas outlet is constant at \( u_{out,g} = 511.2 \) kg h\(^{-1}\).

![Fig. 1. Available numbers of moles in the gas phase and inlet flow rate of \( \text{Cl}_2 \). The solid lines indicate simulated “true” values, while the markers indicate noisy measurements.](image)

The objective in this example is to reconstruct the numbers of moles in the liquid phase using the available measurements in both phases. The reaction system involves the mass transfers of \( \text{Cl}_2 \) and HCl (\( p_m = 2 \)) and two reactions in the liquid phase (\( R = 2 \)). The two mass transfers are computed from the gas phase, and thus \( p_m = p_m = 2 = p_m \). Since \( S_{l,a} + S_{g,a} = 2 + 3 > R + p_m \), rank \( (N_{l,a}^T W_{m_l,t,a}) \) = 2 = \( R + p_m \), and rank \( W_{m_g,g,a} \) = 2 = \( p_m \). Theorem 4 can be applied to reconstruct the unmeasured numbers of moles in the liquid phase as shown in Figure 3.

**VII. Conclusions**

This paper has shown that open F–F reaction systems can be described by \( R + 2p_m + p_l + p_g + 2 \) reaction, mass-transfer
and flow variants instead of the $S_l + S_g$ original states. Conditions have been derived under which the transformed model is indeed a minimal state representation. Furthermore, the transformed model separates the effects of reaction and mass transfer. Note that the reaction and mass-transfer rates (and not the concentrations) are responsible for the observed fast and slow dynamic effects in a reaction system. Hence, a model expressed in terms of reaction and mass-transfer variants can directly exhibit the fast and slow modes, thereby allowing further reduction (beyond the minimal order) by eliminating the fast modes using singular perturbation theory.

The unmeasured concentrations can be reconstructed without knowledge of reaction kinetics and mass-transfer rates if at least $R + p_m$ concentrations can be measured. In an open reactor, it is necessary to also measure the inlet and outlet flow rates.

**REFERENCES**


