Extents of Reaction and Flow for Homogeneous Reaction Systems with Inlet and Outlet Streams

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For homogeneous reaction systems with inlet and outlet streams, this article proposes a linear transformation of the number of moles vector into three distinct parts, namely, the reaction variants, the inlet-flow variants, and the reaction and inlet-flow invariants. The transformed states can be interpreted physically as (i) the amount of material contributed by each reaction and still present in the reactor (extents of reaction), (ii) the amount of material contributed by each inlet stream and still present in the reactor (extents of inlet flow), and (iii) the fraction of the initial conditions that has left the reactor (extent of outlet flow). Furthermore, several implications of being able to compute the extents of reaction and inlet flow are discussed. The methodology is illustrated in simulation via the ethanolysis of phthalyl chloride. © 2010 American Institute of Chemical Engineers *AIChE J,* 56: 2873–2886, 2010
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Introduction

The concept of extent or advancement of reaction is very useful to describe the behavior of chemical reactions. For a particular reaction, the change in extent of reaction is given by the change in the number of moles of any species due to that reaction divided by the corresponding stoichiometric coefficient. The rate of a reaction can be expressed in terms of its extent of reaction, i.e., independently of the various concentrations in the reaction systems.[1] This fact is used to express reaction progress[2,3] and handle chemical equilibrium.[4] However, it is often difficult to compute physically meaningful extents of reaction from concentration measurements due to (i) couplings between reactions, and (ii) material exchange via mass transfer and inlet and outlet streams.

In homogeneous batch reactors, the chemical reactions take place in a single phase in a closed vessel, i.e., there is no material exchanged between phases or with the surroundings. Individual extents of reaction, labeled batch extents of reaction, can be obtained as the coupling between reactions can be handled using stoichiometric information.[5] In contrast, open homogeneous reaction systems, such as semi-batch reactors and continuous stirred-tank reactors (CSTR), exchange material with the surroundings through inlet and possibly outlet streams. As the numbers of moles also change because of the presence of inlet and outlet streams, the concept of batch extents of reaction is not directly applicable.

The objective of this work is the computation of extents of reaction for open homogeneous reactions systems, thus leading to the possibility of investigating the kinetics of each

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reaction individually and independently of the inlet and outlet streams. Material balance equations describe the time evolution of the numbers of moles and contain information regarding the stoichiometry and kinetics of the reaction system as well as operating conditions such as reactor type, initial conditions, inlet concentrations and flowrates, and outlet flowrates. In the study of reaction systems, it is important to distinguish between states that evolve with reaction progress, labeled reaction variants, and states that do not, labeled reaction invariants. As expected, the reaction invariants are independent of the reactions but, unfortunately, the reactions variants do not only represent the contribution of the reactions as they are also affected by inlet and outlet streams.[5–7] Recently, Srinivasan et al.[8] proposed a nonlinear transformation to reaction variants, flow variants, and reaction and flow invariants. However, in all these studies, the reaction variants and invariants are merely mathematical quantities that describe a space rather than individual true extents of reaction. Only in batch reactors, due to absence of inlet and outlet streams, does each reaction variant, upon decoupling using stoichiometric information, correspond to the extent of a particular reaction.

The fact that the reaction variants in batch reactors represent true extents of reaction has been used for modeling reaction systems. Bonvin and Rippin[9] used reaction variants in batch reactors for the determination of stoichiometries without knowledge of reaction kinetics. Amrhein et al.[10,11] used the concept of reaction variants to transform measured concentration and spectral data and build calibration models using reference samples from ongoing reactions. The key models idea therein is to transform measured data in such a way that the contribution of the (unknown) reactions can be separated from the other effects. The objective is kinetic investigation for each reaction individually, i.e., independently of the contribution of the other reactions and of operating conditions such as initial conditions, inlet concentrations, and flowrates.[12,13] Expressed differently, one would like to be able to analyze data measured in an open reactor as if they resulted from a batch reactor. Furthermore, the property of decoupled reaction variants has several implications: (i) one can compare the dynamics of the various reactions and, if appropriate, neglect some compared to others, thus leading to model reduction,[14–16] (ii) sensitivity analysis between a reaction rate and the corresponding kinetic parameters can be performed without having to deal with the complete model of the reaction system,[17–19] and (iii) possibility to perform efficient parameter estimation, one reaction at a time and independently of the inlet and outlet streams.[20,21]

As already mentioned, this article considers the case of open homogeneous reaction systems. The mathematical three-way decomposition of the numbers of moles into reaction variants, flow variants, and reaction and flow invariants proposed by Srinivasan et al.,[8] will be simplified and extended. The simplification results from the redundant mass balance equation, as mass can be computed from the numbers of moles and molecular weights of the various species. The extension eliminates the effect of the initial conditions from the reaction variants and flow variants, thus leading to true extents. This new linear transformation uses only static information regarding the stoichiometry, the inlet composition and the initial conditions and, furthermore, it does not require any constitutive relationships such as kinetic expressions. Moreover, in contrast to the original nonlinear transformation of Srinivasan et al.,[8] the proposed extension enables physical interpretation of the reaction variants as extents of reaction, of the inlet-flow variants as extents of inlet flow, and of one of the reaction and inlet-flow invariants as extent of outlet flow, respectively. Note that this linear transformation can be performed independently of the energy balance.

The article is organized as follows. The first section presents the mole balance equations for open homogeneous reaction systems. The next section describes the reaction space mathematically using a two-way and a three-way decomposition. Then, an extension of the three-way decomposition is proposed and used to derive the concepts of extents of reaction and of inlet and outlet flows. Several implications of this linear transformation are briefly discussed. Then, the computation of the various extents from measured data is illustrated in simulation via the ethanolysis of phthalyl chloride in batch, semi-batch, and continuous modes. The article ends up with conclusions.

Mole Balance Equations for Homogeneous Reaction Systems

The mole balance equations for a homogeneous reaction system involving S species, R reactions, p inlet streams, and one outlet stream can be written generically as follows:

$$\dot{\mathbf{n}}(t) = \mathbf{N}^{\mathrm{T}} V(t)\mathbf{r}(t) + \mathbf{W}_{\mathrm{in}}\mathbf{u}_{\mathrm{in}}(t) - \frac{u_{\mathrm{out}}(t)}{m(t)}\mathbf{n}(t), \qquad \mathbf{n}(0) = \mathbf{n}_0, \quad (1)$$

where $\mathbf{n}$ is the S -dimensional vector of numbers of moles, $\mathbf{r}$ the R-dimensional reaction rate vector, $\mathbf{u}_{\mathrm{in}}$ the p-dimensional inlet mass flowrate vector, u_{out} the outlet mass flowrate, V and m the volume and mass of the reaction mixture, $\mathbf{N}$ the $R \times S$ stoichiometric matrix, $\mathbf{W}_{\mathrm{in}} = \mathbf{M}_{\mathrm{w}}^{-1}\mathbf{W}_{\mathrm{in}}$ the $S \times p$ inlet-composition matrix with $\mathbf{M}_w$ the S-dimensional diagonal matrix of molecular weights and $\check{\mathbf{w}}_{\mathrm{in}} = [\,\check{\mathbf{w}}_{\mathrm{in}}^{1}, \ldots, \check{\mathbf{w}}_{\mathrm{in}}^{p}]$ with $\check{\mathbf{w}}_{\mathrm{in}}^{j}$ being the S-dimensional vector of weight fractions of the jth inlet stream, and $\mathbf{n}_0$ the S-dimensional vector of initial numbers of moles. The flowrates $\mathbf{u}_{\mathrm{in}}(t)$ and $u_{\mathrm{out}}(t)$ are considered as independent (input) variables in Eq. 1. The way these variables are adjusted depends on the particular experimental situation; for example, some elements of $\mathbf{u}_{\mathrm{in}}$ can be adjusted to control the temperature in a semi-batch reactor, or u_{out} can be a function of the inlet flows in a constant-volume reactor. The continuity equation (or total mass balance) is given by:

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

where $\mathbf{1}_p$ is the p-dimensional vector filled with ones and m_0 the initial mass. However, the mass $m(t)$ can also be computed from the numbers of moles as

$$m(t) = \mathbf{1}_S^{\mathrm{T}}\,\mathbf{M}_w\,\mathbf{n}(t). \quad (3)$$

From the relationships $\mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{N}^{\mathrm{T}} = \mathbf{0}_R$ and $\mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{W}_{\mathrm{in}} = \mathbf{1}_p^{\mathrm{T}}$, Eq. 2 can be obtained by differentiation of Eq. 3. Hence, the continuity equation Eq. 2 becomes redundant.

Model (1) is simply a mole balance for a homogeneous single-phase reaction system with several inlet streams and

Table 1. Models of Batch Reactor, Semi-batch Reactor, CSTR During Transient, and CSTR at Steady State

Case	Reactor Type	Model
1	Batch ($\mathbf{u}_{\text{in}} = \mathbf{0}$, $u_{\text{out}} = 0$)	$\dot{\mathbf{n}}(t) = \mathbf{N}^{\text{T}}\, V(t)\, \mathbf{r}(t)$
2	Semi-batch ($u_{\text{out}} = 0$)	$\dot{\mathbf{n}}(t) = \mathbf{N}^{\text{T}}\, V(t)\, \mathbf{r}(t) + \mathbf{W}_{\text{in}}\, \mathbf{u}_{\text{in}}(t)$
3	CSTR ($V = \text{cst}$)	$\dot{\mathbf{n}}(t) = \mathbf{N}^{\text{T}}\, V\, \mathbf{r}(t) + \mathbf{W}_{\text{in}}\, \mathbf{u}_{\text{in}}(t) - \frac{u_{\text{out}}(t)}{m(t)}\, \mathbf{n}(t)$
4	CSTR@SS ($V = \text{cst}$, $\dot{\mathbf{n}} = \mathbf{0}$)	$\mathbf{0} = \mathbf{N}^{\text{T}}\, V\, \mathbf{r} + \mathbf{W}_{\text{in}}\, \mathbf{u}_{\text{in}} - \frac{u_{\text{out}}}{m}\, \mathbf{n}$

SS, steady state.

one outlet stream. The model holds for single-phase reaction systems, both gas and liquid, isothermal or not, as the specificities regarding the reactor type and its operation are contained in the volume $V(t)$, the reaction rate vector $\mathbf{r}(t)$, and the specified inlet and outlet streams $\mathbf{u}_{\text{in}}(t)$ and $u_{\text{out}}(t)$. Because the transformations developed in the next sections need only information regarding the stoichiometric matrix $\mathbf{N}$, the inlet-composition matrix $\mathbf{W}_{\text{in}}$ and the initial conditions $\mathbf{n}_0$, these specificities do not play any role in the transformations. However, for the sake of completeness, these specificities for both gas- and liquid-phase reaction systems are discussed in Appendix A. The mole balance equations for four common reactor types, namely batch reactor, semi-batch reactor, CSTR during transient, and CSTR at steady state are summarized in Table 1.

Throughout this article, the R reactions and p inlets are assumed, without loss of generality, to be independent:

Definition 1 (Independent reactions). *R reactions are said to be independent if (i) the rows of* $\mathbf{N}$ *(stoichiometries) are linearly independent, i.e.*, rank ($\mathbf{N}$) = R, *and (ii) there exists some finite time interval for which the reaction rate profiles* $\mathbf{r}(t)$ *are linearly independent, i.e.* $\boldsymbol{\beta}^{\text{T}}\mathbf{r}(t) = 0 \Leftrightarrow \boldsymbol{\beta} = \mathbf{0}_R$.

Definition 2 (Independent inlets). *p inlet streams are said to be independent if (i) the columns of* $\mathbf{W}_{\text{in}}$ *are linearly independent, i.e.*, rank($\mathbf{W}_{\text{in}}$) $= p$, *and (ii) there exists some finite time interval for which the inlet mass flowrate profiles* $\mathbf{u}_{\text{in}}(t)$ *are linearly independent, i.e.*, $\boldsymbol{\beta}^{\text{T}}\mathbf{u}_{\text{in}}(t) = 0 \Leftrightarrow \boldsymbol{\beta} = \mathbf{0}_p$.

Extents of reaction

For a reaction system with S species and R independent reactions, the change in extent of reaction for the ith reaction, $d\xi_i$, is defined as:[2]

$$d\xi_i := \frac{dn_{s,i}}{\nu_{s,i}}, \quad \forall s = 1, \ldots, S, \quad \forall i = 1, \ldots, R, \tag{4}$$

where $dn_{s,i}$ is the variation of the number of moles of the sth species caused by the ith reaction and $\nu_{s,i}$ the corresponding stoichiometric coefficient. Note that this definition focuses on the reaction and is independent of the reactor type.

The definition of extent of reaction in Eq. 4 can be directly applied to reactors without outlet stream (batch or semi-batch), for which the extent of ith reaction $\xi_i(t)$ satisfies:

$$\dot{\xi}_i(t) = V(t)\; r_i(t), \quad \xi_i(0) = 0. \tag{5}$$

In reactors with an outlet stream, the outlet removes a certain amount of the species present in the reactor. Hence, the number of moles of the sth species caused by the ith reaction needs to account for the outlet term. A mole balance for $n_{s,i}$ involving the reaction and outlet terms gives:

$$\dot{n}_{s,i} = \nu_{s,i}\, V\, r_i - \frac{u_{\text{out}}}{m}\, n_{s,i}. \tag{6}$$

Combining Eqs. 4 and 6 allows expressing the extent of reaction $\xi_i(t)$ that considers only the material still in the reactor:

$$\dot{\xi}_i(t) = V(t)\; r_i(t) - \frac{u_{\text{out}}(t)}{m(t)}\, \xi_i(t), \qquad \xi_i(0) = 0. \tag{7}$$

Note that the definition in Eq. 7 also encompasses that in Eq. 5 for reactors with no outlet stream [$u_{\text{out}}(t) = 0$]. Note also that the kinetics to be investigated at a given time depend on the species present in the reactor at that time, and not on the total amount of material that has been in the reactor. In other words, the extents of reaction $\xi_i(t)$, $i = 1,\ldots,R$, in Eq. 7 represent precisely what is needed for kinetic investigation.

Equations 5 and 7 describe the extents of reaction in a reactor without and with an outlet stream, respectively. However, the objective of this study is not to compute the R-dimensional vector of extents $\boldsymbol{\xi}(t)$ from Eqs. 5 or 7 but from $\mathbf{n}(t)$, i.e., without kinetic information.

Mathematical Reaction Space

This section introduces the concept of reaction variants and invariants. It will be shown that the S-dimensional space in which the numbers of moles evolve can be split into an R-dimensional reaction space and an $(S - R)$-dimensional reaction invariant space.

Definition 3 (Reaction variants). *Any set of R linearly independent variables that evolve in the reaction space constitutes a reaction variant set.*

Definition 4 (Reaction invariants). *Any set of* $(S - R)$ *linearly independent variables that evolve in the space orthogonal to the reaction space constitutes a reaction invariant set.*

Reaction variants can be abstract quantities or, conversely, have a clear physical meaning as in the case of batch extents of reaction. The objective of this work is to compute physically meaningful reaction variants for homogeneous reaction systems with inlet and outlet streams.

Two-way decomposition: reaction variants and invariants

The two-way decomposition found in the literature[6] transforms the space of numbers of moles into mutually orthogonal reaction variant and reaction invariant spaces, as illustrated in Figure 1a. Indeed, the linear transformation

$$\mathbf{n} \longrightarrow \begin{bmatrix} \mathbf{y}_r \\ \mathbf{y}_{iv} \end{bmatrix} = \begin{bmatrix} \mathbf{N}^{\text{T}+} \\ \mathbf{P}^{\text{T}} \end{bmatrix} \mathbf{n} \tag{8}$$

brings Eq. 1 to:

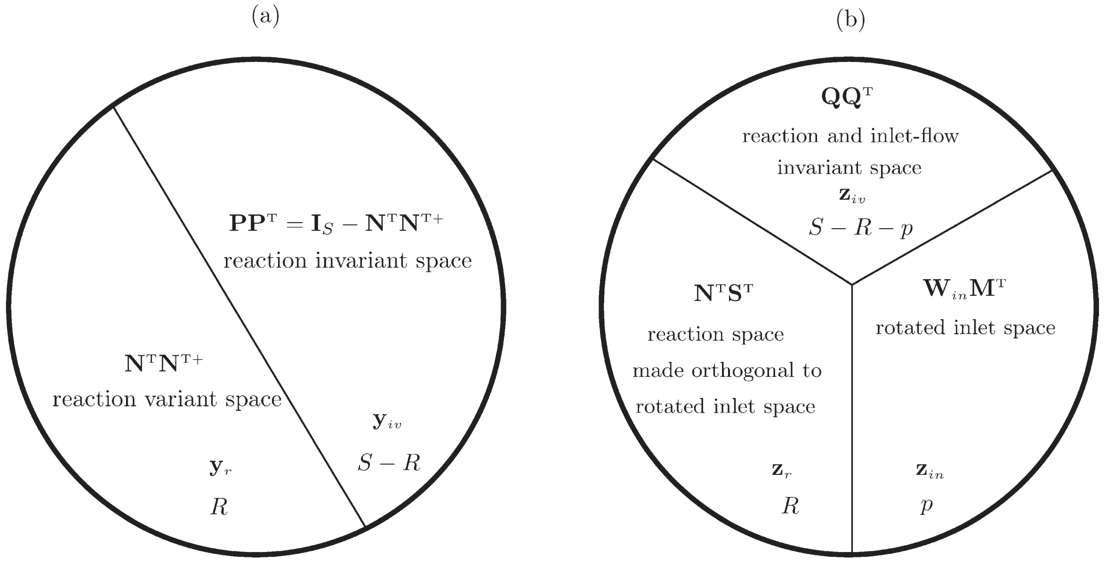

Figure 1. (a) Mathematical two-way decomposition (M2D) and (b) mathematical three-way decomposition (M3D).

M2D decomposes the S-dimensional space of numbers of moles into the R-dimensional reaction variant space and the $(S - R)$-dimensional reaction invariant space. The two spaces are orthogonal to each other with $\mathbf{N}^T\mathbf{N}^{T+}$ 1 + $\mathbf{PP}^T = \mathbf{I}_S$. M3D decomposes the S-dimensional space of numbers of moles into an R-dimensional reaction space, a p-dimensional inlet-flow space, and an $(S - R - p)$-dimensional reaction and inlet-flow invariant space. All spaces are orthogonal to each other with $\mathbf{N}^T\mathbf{S}^T + \mathrm{W}_{in}\mathrm{M}^T + \mathbf{QQ}^T = \mathbf{I}_S$.

$$\begin{aligned}
\dot{\mathbf{y}}_r &= V\mathbf{r} + \mathbf{N}^{T+}\mathbf{W}_{in}\mathbf{u}_{in} - \frac{u_{out}}{m}\mathbf{y}_r, & \mathbf{y}_r(0) &= \mathbf{N}^{T+}\mathbf{n}_0, \\
& & &\text{(reaction variants)} \\
\dot{\mathbf{y}}_{iv} &= \mathbf{P}^T\mathbf{W}_{in}\mathbf{u}_{in} - \frac{u_{out}}{m}\mathbf{y}_{iv}, & \mathbf{y}_{iv}(0) &= \mathbf{P}^T\mathbf{n}_0, \\
& & &\text{(reaction invariants)}
\end{aligned} \tag{9}$$

where "+" indicates the Moore-Penrose pseudo-inverse of a matrix, $\mathbf{y}_r$ is the R-dimensional vector of reaction variants, and $\mathbf{y}_{iv}$ is the $(S - R)$-dimensional vector of reaction invariants, both expressed in kmol. $\mathbf{P}$ is an $S \times (S - R)$ matrix describing the null space of $\mathbf{N}$, i.e., $\mathbf{N}\ \mathbf{P} = \mathbf{0}_{R\times(S-R)}$. The numbers of moles $\mathbf{n}$ in the reactor at time t can be computed from $\mathbf{n}_0$, $\mathbf{y}_r(t)$ and $\mathbf{y}_{iv}(t)$ as follows:

$$\mathbf{n}(t) = \mathbf{N}^T\mathbf{y}_r(t) + \mathbf{P}\,\mathbf{y}_{iv}(t). \tag{10}$$

Equation 9 shows that the reaction term $\mathbf{r}$ affects only the reaction variants $\mathbf{y}_r$. However, as the reaction variants also depend on the inlet and outlet streams, they cannot be interpreted as extents of reaction. Hence, it would be useful to remove the effect of the inlet and outlet streams from the reaction variants, which is the essence of the three-way decomposition introduced in the next subsection.

Three-way decomposition: reaction variants, inlet-flow variants, and invariants

We look for a linear transformation that splits $\mathbf{n}$ into the three parts $\mathbf{z}_r$, $\mathbf{z}_{in}$, and $\mathbf{z}_{iv}$,

$$\mathbf{n} \longrightarrow \begin{bmatrix} \mathbf{z}_r \\ \mathbf{z}_{in} \\ \mathbf{z}_{iv} \end{bmatrix} = \begin{bmatrix} \mathbf{S}^T \\ \mathbf{M}^T \\ \mathbf{Q}^T \end{bmatrix} \mathbf{n}, \tag{11}$$

such that Eq. 1 becomes:

$$\begin{aligned}
\dot{\mathbf{z}}_r &= \underbrace{\mathbf{S}^T\mathbf{N}^T}_{\mathbf{I}_R} V\mathbf{r} + \underbrace{\mathbf{S}^T\mathbf{W}_{in}}_{\mathbf{0}_{R\times p}}\mathbf{u}_{in} - \tfrac{u_{out}}{m}\mathbf{z}_r, & \mathbf{z}_r(0) &= \mathbf{S}^T\mathbf{n}_0, \\
\dot{\mathbf{z}}_{in} &= \underbrace{\mathbf{M}^T\mathbf{N}^T}_{\mathbf{0}_{R\times R}} V\mathbf{r} + \underbrace{\mathbf{M}^T\mathbf{W}_{in}}_{\mathbf{I}_p}\mathbf{u}_{in} - \tfrac{u_{out}}{m}\mathbf{z}_{in}, & \mathbf{z}_{in}(0) &= \mathbf{M}^T\mathbf{n}_0, \\
\dot{\mathbf{z}}_{iv} &= \underbrace{\mathbf{Q}^T\mathbf{N}^T}_{\mathbf{0}_{(S-R-p)\times R}} V\mathbf{r} + \underbrace{\mathbf{Q}^T\mathbf{W}_{in}}_{\mathbf{0}_{(S-R-p)\times p}}\mathbf{u}_{in} - \tfrac{u_{out}}{m}\mathbf{z}_{iv}, & \mathbf{z}_{iv}(0) &= \mathbf{Q}^T\mathbf{n}_0,
\end{aligned} \tag{12}$$

where $\mathbf{S}$, $\mathbf{M}$, and $\mathbf{Q}$ are matrices of dimensions $S \times R$, $S \times p$, and $S \times (S - R - p)$, respectively. These matrices are constructed so as to fulfill the conditions shown under the braces in Eq. 12, for example, $\mathbf{S}^T\mathbf{N}^T = \mathbf{I}_R$. The variables $\mathbf{z}_r$, $\mathbf{z}_{in}$, and $\mathbf{z}_{iv}$ are the reaction variants, the inlet-flow variants, and the reaction and inlet-flow invariants, respectively. Srinivasan et al.[8] proposed a nonlinear transformation that satisfies the conditions given in Eq. 12. Unfortunately, the variables $\mathbf{z}_r(t)$ and $\mathbf{z}_{in}(t)$ cannot be interpreted as the extents of reaction and extents of inlet flow at time t since the initial conditions $\mathbf{z}_r(0)$ and $\mathbf{z}_{in}(0)$ are nonzero.

Theorem 1. *Consider a homogeneous reaction system involving S species, R independent reactions, p independent* *inlets and one outlet, and let* rank $([\mathbf{N}^{\mathrm{T}}, \mathbf{W}_{\mathrm{in}}]) = R + p$. *Then, the linear transformation*

$$\mathbf{n} \longrightarrow \begin{bmatrix} \mathbf{z}_r \\ \mathbf{z}_{\mathrm{in}} \\ \mathbf{z}_{\mathrm{iv}} \end{bmatrix} = \begin{bmatrix} \mathbf{S}^{\mathrm{T}} \\ \mathbf{M}^{\mathrm{T}} \\ \mathbf{Q}^{\mathrm{T}} \end{bmatrix} \mathbf{n} \tag{13}$$

brings Eq. 1 *to:*

$$\begin{aligned} \dot{\mathbf{z}}_r &= V\mathbf{r} - \tfrac{u_{\mathrm{out}}}{m}\mathbf{z}_r, & \mathbf{z}_r(0) &= \mathbf{S}^{\mathrm{T}}\mathbf{n}_0, & &(\textit{reaction variants}) \\ \dot{\mathbf{z}}_{\mathrm{in}} &= \mathbf{u}_{\mathrm{in}} - \tfrac{u_{\mathrm{out}}}{m}\mathbf{z}_{\mathrm{in}}, & \mathbf{z}_{\mathrm{in}}(0) &= \mathbf{M}^{\mathrm{T}}\mathbf{n}_0, & &(\textit{inlet-flow variants}) \\ \dot{\mathbf{z}}_{\mathrm{iv}} &= -\tfrac{u_{\mathrm{out}}}{m}\mathbf{z}_{\mathrm{iv}}, & \mathbf{z}_{\mathrm{iv}}(0) &= \mathbf{Q}^{\mathrm{T}}\mathbf{n}_0. & &(\textit{reaction and inlet-flow invariants}) \end{aligned} \tag{14}$$

$\mathbf{z}_r$ *is the R-dimensional vector of reaction variants expressed in kmol*, $\mathbf{z}_{\mathrm{in}}$ *the p-dimensional vector of inlet-flow variants expressed in kg, and* $\mathbf{z}_{iv}$ *the* $(S - R - p)$*-dimensional vector of reaction and inlet-flow invariants expressed in kmol. The matrices* $\mathbf{S}$, $\mathbf{M}$, *and* $\mathbf{Q}$ *are computed using the algorithm given in Appendix D. The numbers of moles* $\mathbf{n}$ *in the reactor at time t can be computed from* $\mathbf{z}_r(t)$, $\mathbf{z}_{\mathrm{in}}(t)$, and $\mathbf{z}_{\mathrm{iv}}(t)$ as follows:

$$\begin{bmatrix} \mathbf{z}_r \\ \mathbf{z}_{\mathrm{in}} \\ \mathbf{z}_{\mathrm{iv}} \end{bmatrix} \longrightarrow \mathbf{n}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{z}_r(t) + \mathbf{W}_{\mathrm{in}}\mathbf{z}_{\mathrm{in}}(t) + \mathbf{Q}\mathbf{z}_{\mathrm{iv}}(t). \tag{15}$$

See Appendix B for proof.

Interpretation. The three-way decomposition illustrated in Figure 1b can be interpreted as follows. $\mathbf{N}^{\mathrm{T}}\mathbf{N}^{\mathrm{T}+}$, $\mathbf{W}_{\mathrm{in}}\mathbf{W}_{\mathrm{in}}^{+}$, and $\mathbf{Q}\mathbf{Q}^{\mathrm{T}}$ represent the reaction, inlet-flow, and reaction and inlet-flow invariant spaces, respectively. By construction, $\mathbf{Q}\mathbf{Q}^{\mathrm{T}}$ is orthogonal to both the reaction and inlet spaces, which leads to $\mathbf{Q}^{\mathrm{T}}\mathbf{N}^{\mathrm{T}} = \mathbf{0}_{(\mathrm{S-R-p}) \times \mathrm{R}}$ and $\mathbf{Q}^{\mathrm{T}}\mathbf{W}_{\mathrm{in}} = \mathbf{0}_{(\mathrm{S-R-p}) \times \mathrm{p}}$ in Eq. 12, and thus $\mathbf{z}_{\mathrm{iv}}$ is independent of $\mathbf{r}$ and $\mathbf{u}_{\mathrm{in}}$. Furthermore, as the reaction and inlet spaces are not orthogonal to each other, the inlet space is rotated to give the rotated inlet space $\mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}}$ that fulfills the conditions $\mathbf{M}^{\mathrm{T}}\mathbf{N}^{\mathrm{T}} = \mathbf{0}_R$ and $\mathbf{M}^{\mathrm{T}}\mathbf{W}_{\mathrm{in}} = \mathbf{I}_p$ so that $\mathbf{z}_{\mathrm{in}}$ is independent of $\mathbf{r}$ and the inlet-flow variants are decoupled. Finally, as the reaction space $\mathbf{N}^{\mathrm{T}}\mathbf{N}^{\mathrm{T}+}$ is not orthogonal to $\mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}}$, the projection $(\mathbf{I}_S - \mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}})$ is introduced to make the reaction space $\mathbf{N}^{\mathrm{T}}\mathbf{S}^{\mathrm{T}}$ orthogonal to the rotated inlet space, thus giving $\mathbf{S}^{\mathrm{T}} = \mathbf{N}^{\mathrm{T}+}(\mathbf{I}_S - \mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}})$ and $\mathbf{S}^{\mathrm{T}}\mathbf{N}^{\mathrm{T}} = \mathbf{I}_R$. It follows that $\mathbf{z}_r$ is independent of $\mathbf{u}_{\mathrm{in}}$ and the reaction variants are decoupled. Note that the vectors $\mathbf{z}_{\mathrm{in}}$ and $\mathbf{z}_{\mathrm{iv}}$ represent the $(S - R)$ reaction invariants that can be computed independently of the reaction rate expressions $\mathbf{r}$. Note also that the effect of the outlet flow is still present in $\mathbf{z}_r$, $\mathbf{z}_{\mathrm{in}}$, and $\mathbf{z}_{\mathrm{iv}}$ as seen in Eq. 14. The linear transformation in Theorem 1 can be visualized by rewriting Eq. 15 with the help of Eq. 13:

$$\mathbf{n} = \left[\mathbf{N}^{\mathrm{T}}\mathbf{S}^{\mathrm{T}} + \mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}} + \mathbf{Q}\mathbf{Q}^{\mathrm{T}}\right]\mathbf{n} = \mathbf{I}_S\,\mathbf{n}. \tag{16}$$

Computing Extents from the Numbers of Moles n(*t*)

The two-way and three-way decompositions presented in the previous section have generated mathematical variants and invariants that are devoid of a direct physical meaning. For example, due to the presence of nonzero initial conditions, the reaction and inlet-flow variants in Eq. 14 cannot be interpreted as individual extents of reaction and inlet flow. This section will propose a linear transformation of these reaction and flow variants to true extents of reaction and flow, thus paving the way to the computation of extents from the numbers of moles $\mathbf{n}(t)$.

Discounting of initial conditions

For computing the extents of reaction and inlet flow, it is necessary to account for the effect of the nonzero initial conditions in Eq. 14. At time 0, one needs to remove the contributions $\mathbf{z}_{r,0} = \mathbf{S}^{\mathrm{T}}\mathbf{n}_0$ and $\mathbf{z}_{\mathrm{in},0} = \mathbf{M}^{\mathrm{T}}\mathbf{n}_0$. However, the effect of the initial conditions reduces with time due the presence of the outlet stream. Hence, one needs to discount the effect of the nonzero initial conditions, which can be done with the introduction of the discounting variable $\lambda(t) \in [0,1]$ as shown next. The resulting linear transformation of $\mathbf{z}_r$, $\mathbf{z}_{\mathrm{in}}$, and $\mathbf{z}_{\mathrm{iv}}$ reads:

$$\begin{bmatrix} \mathbf{z}_r \\ \mathbf{z}_{\mathrm{in}} \\ \mathbf{z}_{\mathrm{iv}} \end{bmatrix} \longrightarrow \begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{\mathrm{in}} \\ \mathbf{x}_{\mathrm{iv}} \end{bmatrix} = \begin{bmatrix} \mathbf{z}_r \\ \mathbf{z}_{\mathrm{in}} \\ \mathbf{z}_{\mathrm{iv}} \end{bmatrix} - \lambda \begin{bmatrix} \mathbf{z}_{r,0} \\ \mathbf{z}_{\mathrm{in},0} \\ \mathbf{z}_{\mathrm{iv},0} \end{bmatrix} \quad \text{with}$$

$$\lambda = \frac{\mathbf{1}_{S-R-p}^{\mathrm{T}}\mathbf{z}_{\mathrm{iv}}}{\mathbf{1}_{S-R-p}^{\mathrm{T}}\mathbf{z}_{\mathrm{iv},0}} \quad \text{and} \quad \mathbf{1}_{S-R-p}^{\mathrm{T}}\mathbf{z}_{\mathrm{iv},0} \neq 0, \tag{17}$$

where $\mathbf{x}_r$ is the R-dimensional vector of extents of reaction, $\mathbf{x}_{\mathrm{in}}$ the p-dimensional vector of extents of inlet flow, and $\mathbf{x}_{\mathrm{iv}}$ the $(S - R - p)$-dimensional vector of reaction and inlet-flow invariants.

*From numbers of moles n(*t*) to extents x(*t*)*

The linear transformation is described in the next theorem. The transformed reaction and inlet-flow invariant space is one-dimensional and can be described by the variable λ. It will be shown that the condition $\mathbf{1}_{S-R-p}^{\mathrm{T}}\mathbf{z}_{\mathrm{iv},0} \neq 0$ is satisfied if and only if the initial numbers of moles $\mathbf{n}_0$ provide additional information to the inlet-composition matrix $\mathbf{W}_{\mathrm{in}}$ or, in mathematical terms, $\mathbf{W}_{\mathrm{in}}$ and $\mathbf{n}_0$ are linearly independent of each other, i.e., $\mathrm{rank}([\mathbf{W}_{\mathrm{in}}\ \mathbf{n}_0]) = p + 1$.

Theorem 2. *Consider a homogeneous reaction system involving S species, R independent reactions, p independent inlets and one outlet, and let* $\mathrm{rank}([\mathbf{N}^{\mathrm{T}}\ \mathbf{W}_{\mathrm{in}}\ \mathbf{n}_0]) = R + p + 1$. *Then, the linear transformation*

$$\mathbf{n} \longrightarrow \begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{\mathrm{in}} \\ \lambda \end{bmatrix} = \begin{bmatrix} \mathbf{S}_0^{\mathrm{T}} \\ \mathbf{M}_0^{\mathrm{T}} \\ \mathbf{q}_0^{\mathrm{T}} \end{bmatrix} \mathbf{n}, \tag{18}$$

with

$$\mathbf{S}_0^{\mathrm{T}} = \mathbf{S}^{\mathrm{T}}(\mathbf{I}_S - \mathbf{n}_0\,\mathbf{q}_0^{\mathrm{T}}), \qquad \mathbf{M}_0^{\mathrm{T}} = \mathbf{M}^{\mathrm{T}}(\mathbf{I}_S - \mathbf{n}_0\,\mathbf{q}_0^{\mathrm{T}}),$$

$$\mathbf{q}_0^{\mathrm{T}} = \frac{\mathbf{1}_{S-R-p}^{\mathrm{T}}\mathbf{Q}^{\mathrm{T}}}{\mathbf{1}_{S-R-p}^{\mathrm{T}}\mathbf{Q}^{\mathrm{T}}\mathbf{n}_0}, \tag{19}$$

brings Eq. 1 *to:*

$$\begin{aligned}
\dot{x}_{r,i} &= V\, r_i - \frac{u_{\text{out}}}{m}\, x_{r,i}, & x_{r,i}(0) &= 0, & \forall\, i &= 1,\ldots,R, \\
&&&&& \textit{(extents of reaction)} \\
\dot{x}_{in,j} &= u_{in,j} - \frac{u_{out}}{m}\, x_{in,j}, & x_{in,j}(0) &= 0, & \forall\, j &= 1,\ldots,p, \\
&&&&& \textit{(extents of inlet flow)} \\
\dot{\lambda} &= -\frac{u_{out}}{m}\, \lambda, & \lambda(0) &= 1. && \textit{(discounting of } \mathbf{n}_0\textit{)}
\end{aligned} \tag{20}$$

$x_{r,i}$ is the extent of reaction corresponding to the ith reaction expressed in kmol, $x_{\text{in},j}$ the extent of inlet flow corresponding to the jth inlet expressed in kg, and λ the scalar dimensionless variable used to discount the effect of the initial conditions. The numbers of moles **n** *in the reactor at time t can be computed from* $\mathbf{x}_r(t)$, $\mathbf{x}_{\text{in}}(t)$, and $\lambda(t)$ as follows:

$$\begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{\text{in}} \\ \lambda \end{bmatrix} \longrightarrow \mathbf{n}(t) = \mathbf{N}^{\text{T}}\mathbf{x}_r(t) + \mathbf{W}_{\text{in}}\mathbf{x}_{\text{in}}(t) + \mathbf{n}_0\lambda(t). \tag{21}$$

See Appendix C for proof.

Remarks. Several remarks are in order:

1. It is convenient to express the transformed system exclusively in terms of extents by introducing the dimensionless scalar extent of outlet flow $x_{\text{out}}(t) = 1 - \lambda(t)$, with which Eq. 21 becomes:

$$\begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{\text{in}} \\ \mathbf{x}_{\text{out}} \end{bmatrix} \longrightarrow \mathbf{n}(t) = \mathbf{n}_0 + \mathbf{N}^{\text{T}}\mathbf{x}_r(t) + \mathbf{W}_{\text{in}}\mathbf{x}_{\text{in}}(t) - \mathbf{n}_0\mathbf{x}_{\text{out}}(t). \tag{22}$$

x_{out} evolves also in the one-dimensional space $\mathbf{n}_0\mathbf{q}_0^{\text{T}}$.

2. The extent of reaction $x_{r,i}$ in Eq. 20 corresponds to ξ_i in Eq. 7.

3. Transformation (18) uses the knowledge of **N**, $\mathbf{W}_{\text{in}}$, and $\mathbf{n}_0$. Note that, compared to the transformation (11), this transformation depends on the initial conditions $\mathbf{n}_0$, hence the subscript 0 in the transformation matrices.

4. The transformed reaction system is of dimension $R + p + 1$ and not S. The $(S - R - p)$ invariant states $\mathbf{x}_{\text{iv}}$ are identically equal to zero and can be discarded:

$$\mathbf{x}_{\text{iv}}(t) = \mathbf{Q}_0^{\text{T}}\mathbf{n}(t) = \mathbf{0}_{S-R-p}, \tag{23}$$

with $\mathbf{Q}_0^{\text{T}} = \mathbf{Q}^{\text{T}}(\mathbf{I}_S - \mathbf{n}_0\mathbf{q}_0^{\text{T}})$.

5. The matrix $(\mathbf{I}_S - \mathbf{n}_0\mathbf{q}_0^{\text{T}})$ removes the contribution of $\mathbf{n}_0$ from $\mathbf{z}_r$, $\mathbf{z}_{\text{in}}$, and $\mathbf{z}_{\text{iv}}$ to obtain $\mathbf{x}_r$, $\mathbf{x}_{\text{in}}$, and $\mathbf{x}_{\text{iv}}$. Hence, $\mathbf{x}_r$ evolves in the R-dimensional space $\mathbf{N}^{\text{T}}\mathbf{S}_0^{\text{T}}$, $\mathbf{x}_{\text{in}}$ in the p-dimensional space $\mathbf{W}_{\text{in}}^{\text{T}}\mathbf{M}_0^{\text{T}}$, and $\mathbf{x}_{\text{iv}}$ in the $(S - R - p - 1)$-dimensional space $\mathbf{Q}\mathbf{Q}_0^{\text{T}}$. λ evolves in the one-dimensional space $\mathbf{n}_0\mathbf{q}_0^{\text{T}}$. Note that the spaces for $\mathbf{x}_r$, $\mathbf{x}_{\text{in}}$, $\mathbf{x}_{\text{iv}}$, and λ are not orthogonal to each other, but they add up to the identity matrix, i.e., $\mathbf{N}^{\text{T}}\mathbf{S}_0^{\text{T}} + \mathbf{W}_{\text{in}}\mathbf{M}_0^{\text{T}} + \mathbf{Q}\mathbf{Q}_0^{\text{T}} + \mathbf{n}_0\mathbf{q}_0^{\text{T}} = \mathbf{I}_S$.

6. It is well known[22] that a nonzero $\mathbf{n}_0$ never lies in the row space of **N**. Thus, the working assumption of Theorem 2, $\text{rank}([\mathbf{N}^{\text{T}}\mathbf{W}_{\text{in}}\ \mathbf{n}_0]) = R + p + 1$, implies $\text{rank}([\mathbf{W}_{\text{in}}\ \mathbf{n}_0]) = p + 1$.

7. In the case where $\mathbf{n}_0$ is a linear combination of the rows of $\mathbf{W}_{\text{in}}$, i.e., $\text{rank}([\mathbf{W}_{\text{in}}\ \mathbf{n}_0]) = p$, $\mathbf{n}_0$ can be modeled by an impulse inlet flowrate for the given $\mathbf{W}_{\text{in}}$. Hence, $\mathbf{z}_{r,0} = \mathbf{0}_R$ and $\mathbf{z}_{\text{in},0} = \mathbf{0}_{\text{p}}$ in the model (14), which generates the extents $\mathbf{z}_r = \mathbf{x}_r$ and $\mathbf{z}_{\text{in}} = \mathbf{x}_{\text{in}}$.

The linear transformation of Theorem 2 is illustrated in Figure 2. The physical interpretation of $\mathbf{x}_r$, $\mathbf{x}_{\text{in}}$, and x_{out} is discussed next.

Extents of Reaction $\boldsymbol{x}_{\text{r}}$ *(kmol):* Equation 20 indicates that the extent of reaction $\boldsymbol{x}_{r,i}$ ($\forall i = 1,\ldots, R$) is decoupled from the other extents. It can be interpreted as the number of moles that is produced by the ith reaction and remains in the reactor. The term $-\frac{u_{\text{out}}}{m}x_{r,i}$ accounts for the material produced by the ith reaction and removed from the reactor.

Extents of Inlet Flow $\boldsymbol{x}_{\text{in}}$ *(kg):* The element $x_{\text{in},j}$ ($\forall j = 1,\ldots,p$) can be interpreted as the mass added by the jth inlet that remains in the reactor. The term $-\frac{u_{\text{out}}}{m}x_{\text{in},j}$ accounts for the material added by the jth inlet that has left the reactor.

Extent of Outlet Flow $\boldsymbol{x}_{\text{out}}$ *(–):* The element x_{out} indicates the fraction of the initial conditions that has been removed from the reactor through the outlet. In the case of no outlet, $x_{\text{out}} = 0$, while with an outlet, $x_{\text{out}}(t)$ goes asymptotically to one.

Special reactor configurations

The extents of reaction and flow for special reactor configurationss such as batch, semi-batch and CSTR reactors are discussed next.

Batch Reactor: In a batch reactor, $p = 0$ and $u_{\text{out}} = 0$. It follows that $x_{\text{out}} = 0$, and Eq. 20 reduces to:

$$\dot{x}_{r,i} = V\, r_i, \quad x_{r,i}(0) = 0, \quad \forall i = 1,\ldots,R. \quad \text{(extents of reaction)} \tag{24}$$

$x_{r,i}$ corresponds to the batch extent of the ith reaction in Eq. 5, i.e., the number of moles converted by the ith reaction. The dynamic system is of order R. The reconstruction of $\mathbf{n}(t)$ is given by:

$$\mathbf{n}(t) = \mathbf{n}_0 + \mathbf{N}^{\text{T}}\mathbf{x}_r(t). \tag{25}$$

Semi-batch Reactor: In a semi-batch reactor, $u_{\text{out}} = 0$. It follows that $x_{\text{out}} = 0$, and Eq. 20 reduces to:

$$\begin{aligned}
\dot{x}_{r,i} &= V\, r_i, \ \ x_{r,i}(0) = 0, \ \forall i = 1,\ldots,R, \ \text{(extents of reaction)} \\
\dot{x}_{\text{in},j} &= u_{\text{in},j}, \ \ x_{\text{in},j}(0) = 0, \ \forall i = 1,\ldots,p. \ \text{(extents of inlet flow)}
\end{aligned} \tag{26}$$

$x_{r,i}$ is the (batch) extent of reaction of the ith reaction. $x_{\text{in},j}$ can be interpreted as the mass added to the reactor by the jth inlet and is labeled the extent of the jth inlet flow. Note that $m(t) = m_0 + \mathbf{1}_p^{\text{T}}\ \mathbf{x}_{\text{in}}(t)$. The dynamic system is of order $R + p$. The reconstruction of $\mathbf{n}(t)$ is given by:

$$\mathbf{n}(t) = \mathbf{n}_0 + \mathbf{N}^{\text{T}}\mathbf{x}_r(t) + \mathbf{W}_{\text{in}}\mathbf{x}_{\text{in}}(t). \tag{27}$$

CSTR: In a CSTR, $u_{\text{out}}(t)$ is computed from $V(t) = \frac{m(t)}{\rho(t)} = V_0$ and Eq. 2 as follows:

$$u_{\text{out}}(t) = \mathbf{1}_p^{\text{T}}\mathbf{u}_{\text{in}}(t) - \dot{\rho}(t)\, V_0, \tag{28}$$

where ρ is the mixture density. The extents of reaction and flow are computed from Eq. 20 and the reconstruction of $\mathbf{n}(t)$

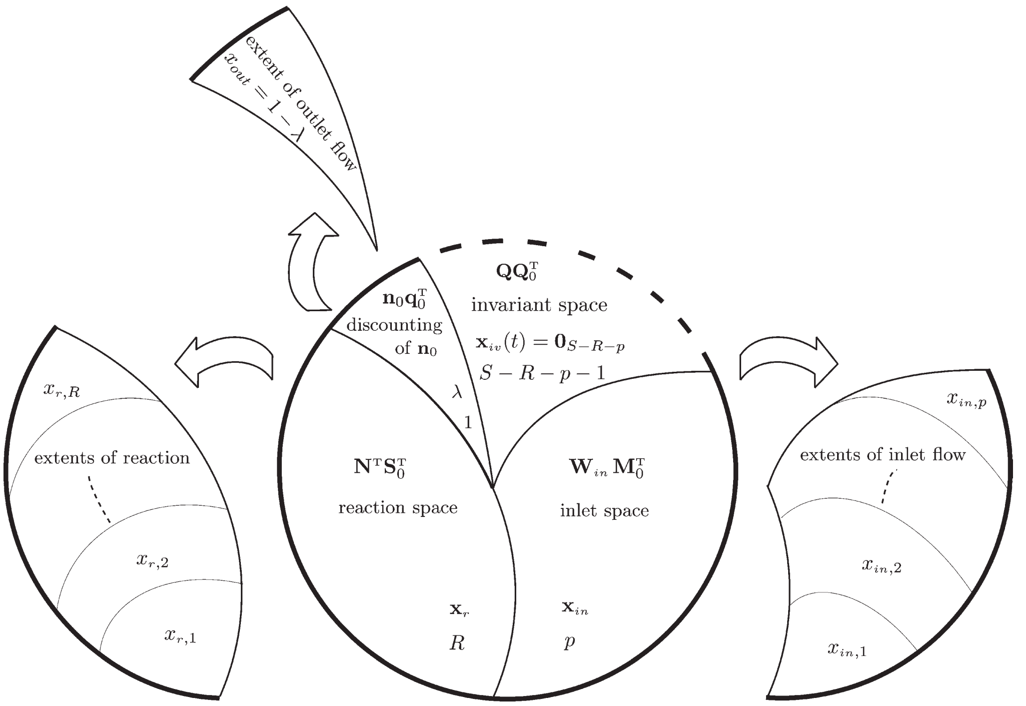

Figure 2. Physical three-way decomposition (P3D).

P3D decomposes the S-dimensional space of numbers of moles into an R-dimensional reaction space, a p-dimensional inlet-flow space, a one-dimensional space describing the discounting of $\mathbf{n}_0$, and an $(S - R - p - 1)$ -dimensional invariant space.

The extents of reaction ($x_{r,i}, i = 1,2,\ldots,R$), extents of inlet flow ($x_{\mathrm{in},j}$, $j = 1,2,\ldots,p$), and extent of outlet flow (x_{out}) are illustrated by the side figures. Note that these spaces are not orthogonal to each other due to the removal of the initial conditions through the matrix $(\mathbf{I}_S - \mathbf{n}_0\mathbf{q}_0^{\mathrm{T}})$, but $\mathbf{N}^{\mathrm{T}}\mathbf{S}_0^{\mathrm{T}} + \mathbf{W}_{\mathrm{in}}\mathbf{M}_0^{\mathrm{T}} + \mathbf{n}_0\mathbf{q}_0^{\mathrm{T}} + \mathbf{Q}\mathbf{Q}_0^{\mathrm{T}} = \mathbf{I}_S$.

is given by Eq. 22. The dynamic system is of order $R + p + 1$. Note that, if the density is constant, $\rho(t) = \rho_0$, $m(t) = m_0$ and $u_{\mathrm{out}}(t) = \mathbf{1}_p^{\mathrm{T}}\,\mathbf{u}_{\mathrm{in}}(t)$. It follows that $\lambda(t)$ can be computed algebraically from the states $\mathbf{x}_{\mathrm{in}}(t)$ as $\lambda(t) = 1 - \frac{\mathbf{1}_p^{\mathrm{T}}\mathbf{x}_{\mathrm{in}}(t)}{m_0}$ and, thus, the state equation for λ can be removed and the dynamic system is of order $R + p$.

Implications of Being Able to Compute x(*t*) from n(*t*)

The linear transformation proposed by Theorem 2 leads to extents of reaction and flow. Several implications are briefly discussed in the following sections.

Identification of reaction systems from measured data

The expressions $V(t)r_i(\mathrm{t})$, $\forall i = 1,\ldots,R$, and $u_{\mathrm{in},j}(t)$, $\forall j = 1,\ldots,p$, can be computed from the measured numbers of moles $\mathbf{n}(t)$ and the knowledge of $\mathbf{N}$, $\mathbf{W}_{\mathrm{in}}$, and $\mathbf{n}_0$ using a differential method.[23] For batch reactors, for example, the product $V(t)\,\mathbf{r}(t)$ can be computed through differentiation of $\mathbf{n}(t)$ and knowledge of $\mathbf{N}$ (see Table 1). However, the same task is more difficult in semi-batch and CSTR reactors because of the contributions of the inlet term $\mathbf{W}_{\mathrm{in}}\mathbf{u}_{\mathrm{in}}(t)$ and outlet term $\frac{u_{\mathrm{out}}(t)}{m(t)}\mathbf{n}(t)$. If these terms are either known or measured, they can be accounted for and the product $V\mathbf{r}$ inferred from $\mathbf{n}(t)$. On the other hand, even if the inlet and outlet terms are unknown, the proposed linear transformation (18) allows computing the individual extents of reaction and flow from the measured $\mathbf{n}$ using an integral method. It is well-known that the integral method has statistical advantages over the differential method in the presence of only a few noisy measurements of $\mathbf{n}$.[23] Then, in subsequent steps, reaction kinetics can be investigated individually for each reaction using for example the incremental identification approach proposed in Brendel et al.[13]

Model reduction

For batch and semi-batch reaction systems, a comparison of Eqs. 1 and 20 indicates that the number of state variables has been reduced from S to $(R + p + 1)$ for general open reaction systems, and even further to R for batch and $(R + p)$ for semi-batch and constant-density CSTR. The model order can also be reduced by eliminating fast modes using, for example, singular perturbation theory.[14,24] As the reactions (and not the numbers of moles) exhibit the fast and slow dynamics behavior, the numbers of moles typically cannot be classified as fast or slow states and Eq. 1 is not suited for application of singular perturbation theory. In contrast, the extents of reaction $\mathbf{x}_r$ in Eq. 20 are direct functions of the reaction rates and, thus, can be separated into fast and slow dynamics.

Parametric sensitivity analysis

Parametric sensitivity is simplified by working with the extents of reaction instead of the numbers of moles since the

Table 2. Reaction Rate Constants (in m^3 $kmol^{-1}$ h^{-1})

κ_1	κ_2	κ_3	κ_4
0.127	0.023	11.97	8.01

extent of reaction $x_{r,i}(t)$ contains all, but also only, information regarding $V(t)r_i(t)$. Another nice feature of the extents of reaction is the fact that they are orthogonal to the inlet space, thereby leading to $\partial \mathbf{x}_r / \partial \mathbf{u}_{in} = \mathbf{0}_{R \times p}$.

Parameter identification

The issue of parameter identification is related to parametric sensitivity. As mentioned above, one can compute the individual extents of reaction and inlet flow from the measured data $\mathbf{n}(t)$. The resulting individual reaction rates $V(t)$ $r_i(t)$, $\forall i = 1,\ldots,R$, can then be used to estimate the kinetic parameters one reaction at a time and independently of the inlet and outlet flow patterns. Furthermore, it has been proposed to test possible model deficiencies by estimating kinetic parameters.[25] Since the stochastic error terms stem mainly from the parametric uncertainty of reaction rates, it is easier to associate stochastic terms to the individual extents of reaction $x_{r,i}$, $i = 1,\ldots,R$, than to $\mathbf{n}$. This way, the search for possible model deficiencies can be limited to the typically nonlinear expressions of reaction rates.

Illustrative Simulated Reaction Example

The implication of being able to compute the extents of reaction and flow from measured data is illustrated through a simulated varying-density isothermal homogeneous reaction system. The reaction system considered is the ethanolysis of phthalyl chloride (A).[26] In two successive irreversible ethanolysis reactions, the desired product phthalyl chloride monoethyl ester (C) and phthalic diethylester (E) are produced from ethanol (B). Both reactions 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 with seven species ($S = 7$) and three independent reactions ($R = 3$):

$$\begin{aligned} \text{R1}: &\quad A + B \xrightarrow{r_1} C + D, \\ \text{R2}: &\quad C + B \xrightarrow{r_2} E + D, \\ \text{R3}: &\quad D + B \overset{r_3}{\rightleftharpoons} F + G. \end{aligned}$$

The stoichiometric matrix is $\mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 1 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 & 0 & 0 \\ 0 & -1 & 0 & -1 & 0 & 1 & 1 \end{bmatrix}$

and the reaction rates obey the mass-action principle: $r_1 = \kappa_1 c_A c_B$, $r_2 = \kappa_2 c_B c_C$, $r_3 = \kappa_3 c_B c_D - \kappa_4 c_F c_G$, with the reaction rate constants κ_i given in Table 2. The molecular weights and densities of the pure species are given in Table 3. The vector of numbers of moles is $\mathbf{n} = [n_A, n_B, n_C, n_D, n_E, n_F, n_G]^T$. As the reactor is considered isothermal, the density of the reaction mixture is computed as $\rho = 1 / \sum_{i=1}^{S} \frac{\breve{w}_i}{\rho_i}$, with $\breve{w}_i$ the weight fraction of species i. Three reactor configurations will be investigated, namely a batch reactor, a semi-batch reactor, and the startup of a CSTR.

Case 1: Batch reactor

0.2 kmol of A and 0.6 kmol of B are initially placed in the reactor and thus $\mathbf{n}_0 = [0.2, 0.6, 0, 0, 0, 0, 0]^T$ kmol. A is the limiting reactant.

Extents of Reaction. The numbers of moles $\mathbf{n}(t)$ are simulated using Eqs. 1, 3, and 29 and are considered as noise-free measured data (see Figure 3a). As the mixture density varies with concentration, the volume varies as well (not shown here). The extents of reaction $\mathbf{x}_r$ are computed from $\mathbf{n}$ using Eq. 18, i.e., without kinetic information. The extents $x_{r,1}$, $x_{r,2}$, and $x_{r,3}$ in Figure 3b correspond to the numbers of moles produced by R1, R2, and R3, respectively. As A is the limiting reactant and is only consumed by R1, $x_{r,1}(t) = n_{A,0} - n_A(t)$ and approaches 0.2 kmol, indicating completion of R1. Species C, which is produced by R1 and consumed by R2, limits R2 shortly after R1 stops. The extent $x_{r,2}$ indicates the number of moles of E that is produced by R2 and also approaches 0.2 kmol, indicating completion of R2. As the forward reaction of R3 is initially faster than the backward reaction, $x_{r,3}$ goes through a maximum before approaching equilibrium. The profile of $x_{r,3}$ corresponds to that of G. The reaction variants computed in this case correspond to the well-known batch extents of reaction.

Case 2: Semi-batch reactor

0.5 kmol of A is initially placed in the reactor, $\mathbf{n}_0 = [0.5, 0.0, 0,0, 0, 0, 0]^T$ kmol. Species B is fed to the reactor with the constant mass flowrate 5.3 kg h^{-1} ($p = 1$), thus leading to $\mathbf{W}_{in} = [0\ 0.0217\ 0\ 0\ 0\ 0\ 0\ ]^T$ kmol kg^{-1} and rank([$\mathbf{N}^T$ $\mathbf{W}_{in}$]) $= R + p = 4$ as required by Theorem 1. The matrices $\mathbf{S}$, $\mathbf{M}$, and $\mathbf{Q}$ are computed using the algorithm given in Appendix D.

Extents of Reaction and Inlet Flow. $\mathbf{n}(t)$ is simulated and considered as measured data. This is illustrated in Figure 4, which also shows the reactor mass computed from $\mathbf{n}$ using Eq. 3. The extents of reaction $\mathbf{x}_r$ and the extent of inlet flow x_{in} are computed using Eq. 18, i.e., without information regarding the kinetics and the inlet flow. As in Case 1, as the reactants A and C are limiting, $x_{r,1}$ and $x_{r,2}$ reach asymptotically 0.5 kmol. Because the forward part of R3 dominates due to feeding of B, the equilibrium of R3 is pushed to the right side, and $x_{r,3}$ increases steadily with time, producing F and G, until full

Table 3. Molecular Weights $M_{w,i}$, in kg $kmol^{-1}$, and Liquid Densities ρ_i, in kg m^{-3}, of the S Pure Species

Species	$M_{w,i}$	ρ_i
A	203	1400
B	46	790
C	212.5	1118
D	36.5	1486
E	222	1118
F	64.5	921.4
G	18	998

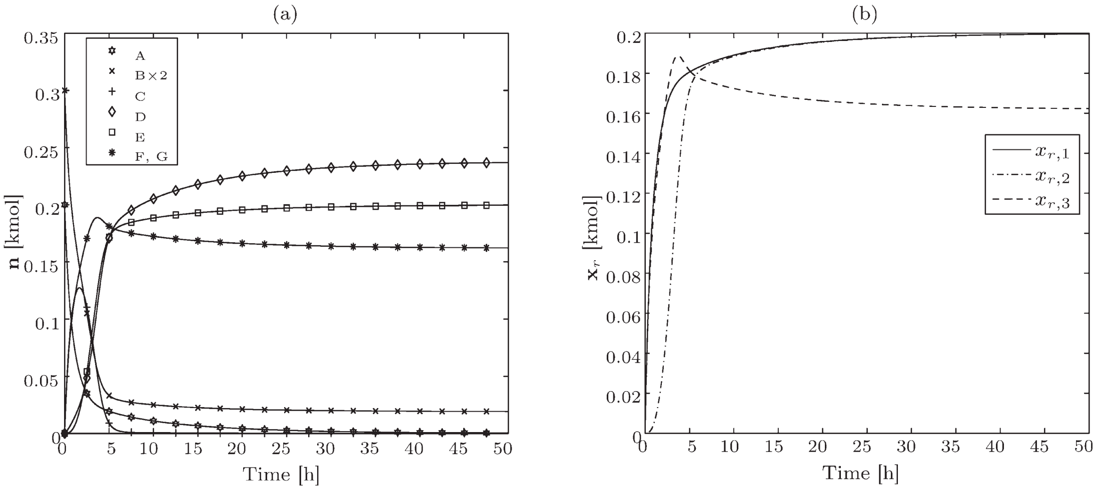

Figure 3. Batch reactor.

Time profiles of (a) the numbers of moles **n**, and (b) the extents of reaction $\mathbf{x}_r$.

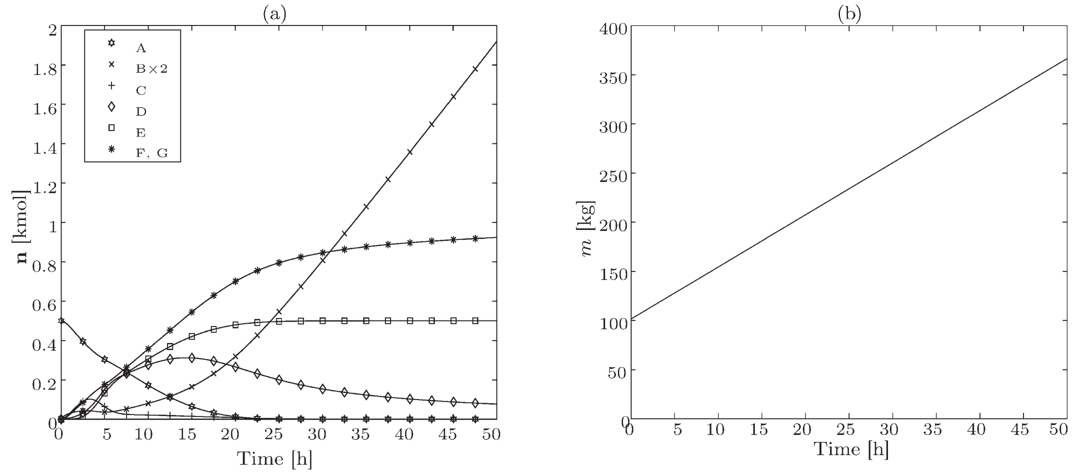

Figure 4. Semi-batch reactor.

Time profiles of (a) the numbers of moles **n**, and (b) the reactor mass m.

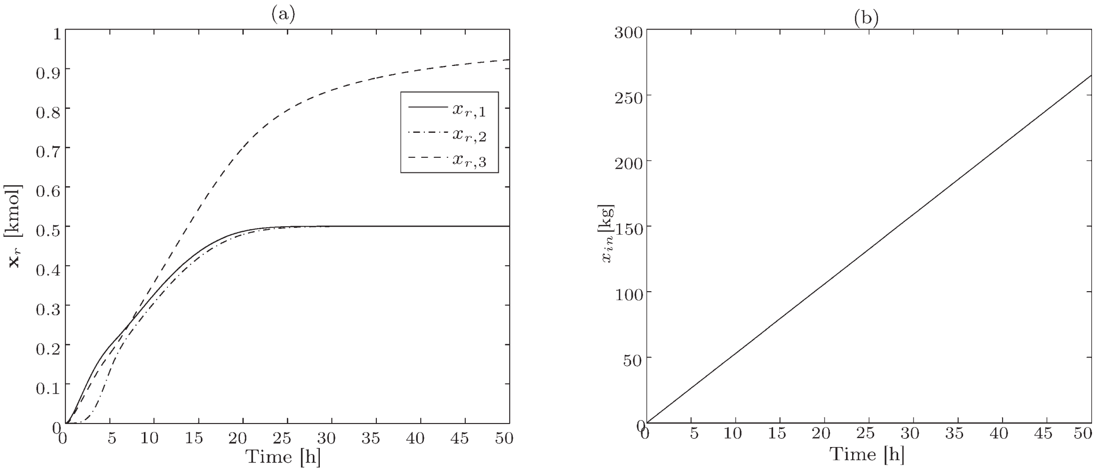

Figure 5. Semi-batch reactor.

Time profiles of (a) the extents of reaction $\mathbf{x}_r$, and (b) the extent of inlet flow x_{in}.

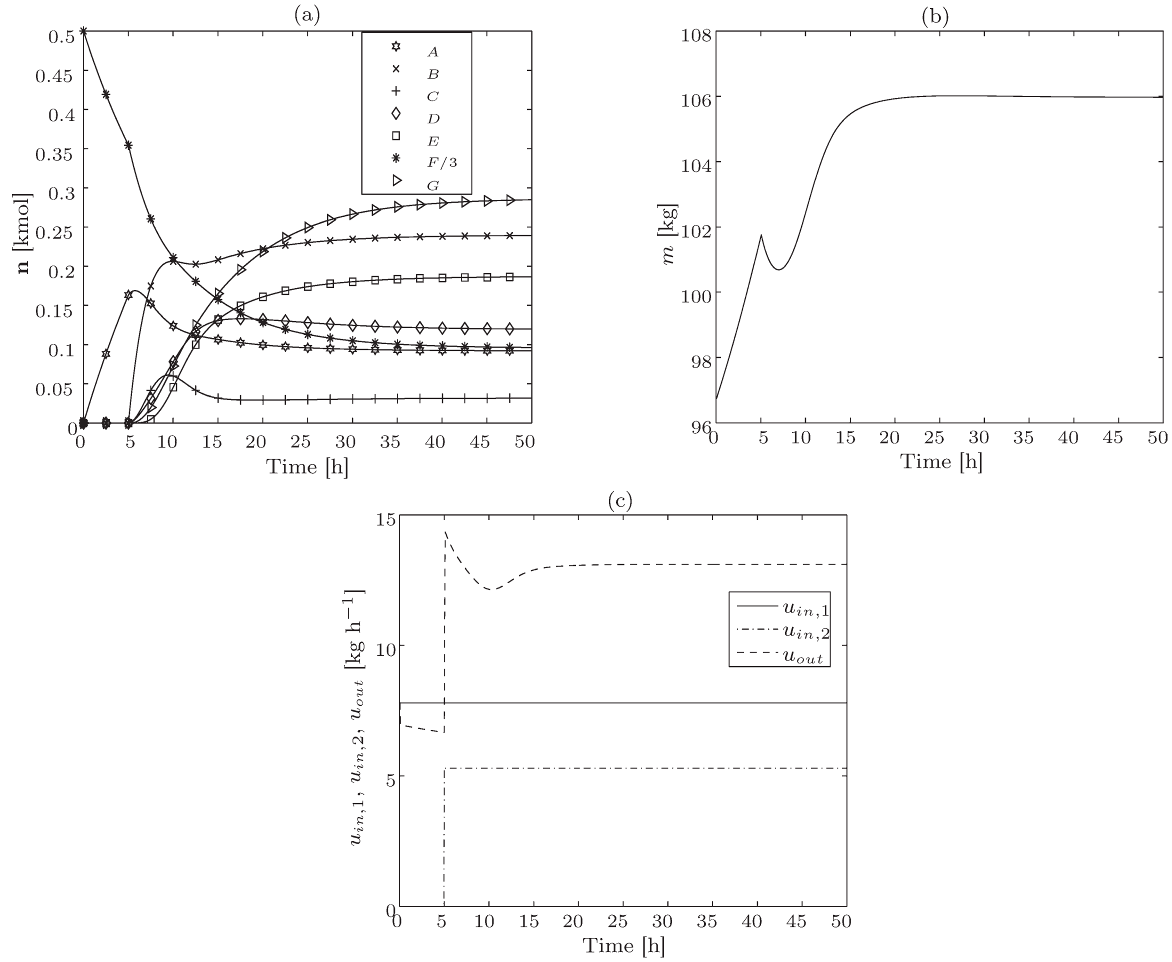

Figure 6. Startup of CSTR.

Time profiles of (a) the numbers of moles $\mathbf{n}$, (b) the reactor mass m, and (c) the inlet and outlet mass flowrates $u_{\text{in},1}$, $u_{\text{in},2}$, and u_{out}.

depletion of D (not shown here). As shown in Figure 5b, x_{in} increases steadily with time due to feeding of B.

Case 3: Startup of CSTR

There are two inlets to the CSTR ($p = 2$): pure phthalyl dichloride A and pure ethanol B, thus leading to $\mathbf{W}_{\text{in}} = \begin{bmatrix} 0.0049 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.0217 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}^{\text{T}}$ kmol kg^{-1} and rank([$\mathbf{N}^{\text{T}}$ $\mathbf{W}_{\text{in}}$]) $= R + p = 5$.

The reactor is initially filled with 1.5 kmol of ethyl chloride (F) and thus $\mathbf{n}_0 = [0, 0, 0, 0, 0, 1.5, 0]^{\text{T}}$ kmol. Species A is fed with the constant mass flowrate 7.8 kg h^{-1}, while feeding of B with the constant mass flowrate 5.3 kg h^{-1} starts after 5 h ($p = 2$). Hence, there is no reaction in the interval [0, 5] h. The time profiles of $\mathbf{n}$ simulated using Eq. 1 are shown in Figure 6a, the mass m computed using Eq. 3 is shown in Figure 6b, and the inlet and outlet streams are shown in Figure 6c. Note that the outlet flowrate varies even when the inlet flows are constant. Indeed, feeding the heavy species A increases the density of the reaction mixture which, according to Eq. 28, decreases the outlet mass flowrate. Addition of the light species B to the reactor after $t = 5$ h initially decreases the density and thus also the reactor mass. Thereafter, the reactions produce heavy species, which increases m.

Mathematical Reaction Space. The transformation matrices $\mathbf{S}$, $\mathbf{M}$, and $\mathbf{Q}$ are calculated using the algorithm given in Appendix D. Transformation (13) is first applied to $\mathbf{n}$ to compute the reaction variants $\mathbf{z}_r$, the inlet-flow variants $\mathbf{z}_{\text{in}}$, and the reaction and flow invariants $\mathbf{z}_{\text{iv}}$ (see Figure 7a–c). Figure 7a shows that all reaction variants take nonzero (positive) values in the time interval [0, 5] h despite the absence of reaction. This behavior results from the effect of the nonzero initial condition $\mathbf{S}^{\text{T}}\mathbf{n}_0$. Similarly, $z_{\text{in},2}$ (corresponding to the feed of B) takes nonzero values in the same time interval despite the absence of feed B. This behavior is due to the effect of the nonzero initial conditions $\mathbf{M}^{\text{T}}\mathbf{n}_0$. Hence, unlike in batch and semibatch reactors, the mathematical reaction variants $\mathbf{z}_r$ and the inlet-flow variants $\mathbf{z}_{\text{in}}$ do not represent physical extents in reaction systems with an outlet stream.

Extents of reaction and flow The matrix $\mathbf{Q}$ and $\mathbf{M}$ are calculated using the algorithm given in Appendix D. As rank([$\mathbf{N}^{\text{T}}$ $\mathbf{W}_{\text{in}}$ $\mathbf{n}_0$]) $= R + p + 1 = 6$ and $\mathbf{1}^{\text{T}}_{S-R-p}\mathbf{Q}^{\text{T}}\mathbf{n}_0 = 0.4160 \neq 0$, Theorem 2 can be applied. The extents of

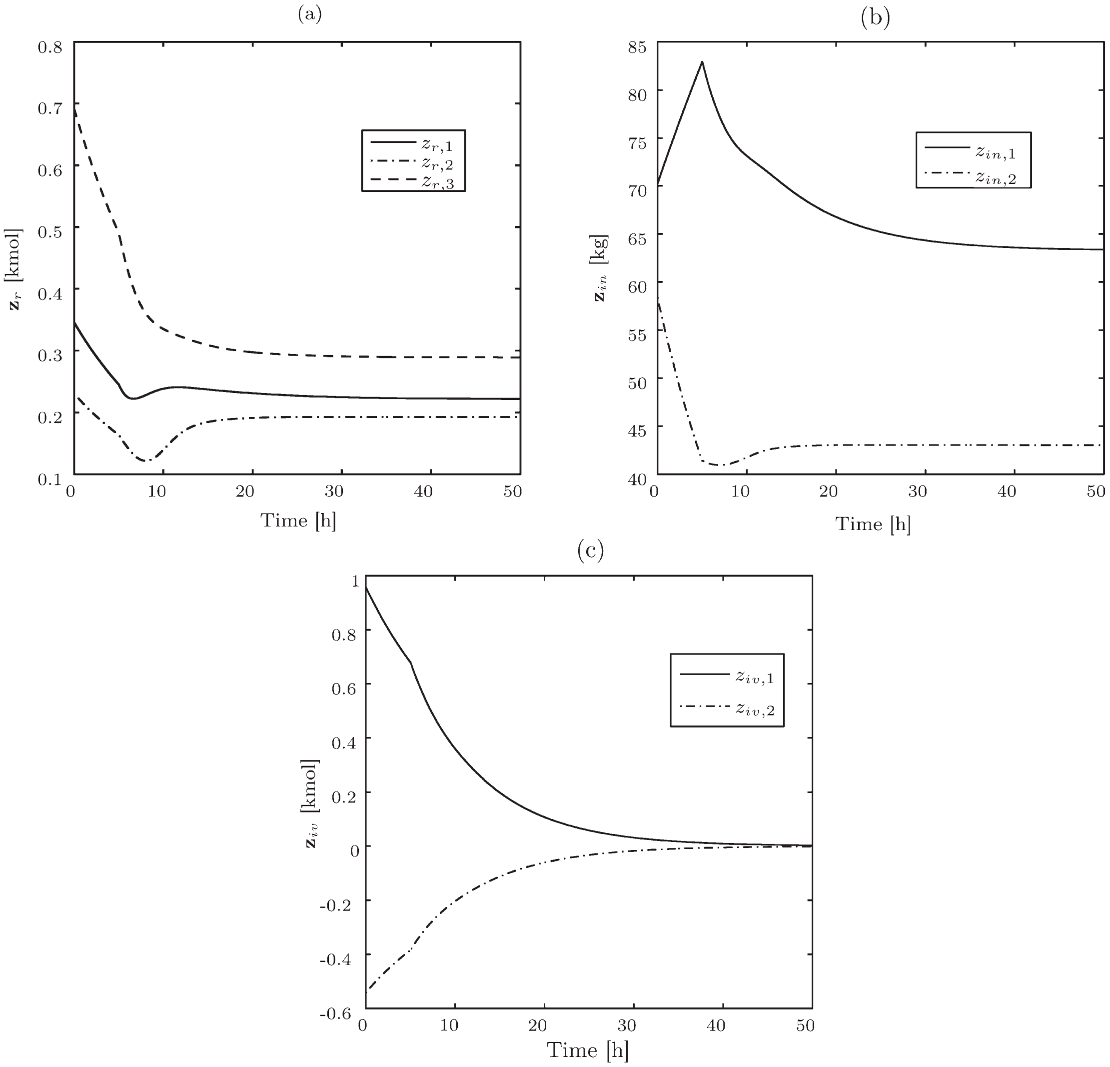

Figure 7. Mathematical variants in the startup of CSTR.

(a) Reaction variants $\mathbf{z}_r$, (b) inlet-flow variants $\mathbf{z}_{\text{in}}$, and (c) reaction and inlet-flow invariants $\mathbf{z}_{\text{iv}}$.

reaction and flow are computed from $\mathbf{n}$ using Eq. 18, i.e., without information regarding the kinetics and the inlet and outlet flows. The results are shown in Figure 8 and discussed in the following sections.

Extents of Reaction. Figure 8a shows the time profiles of the extents of reaction $x_{r,1}$, $x_{r,2}$, and $x_{r,3}$ corresponding to the reactions R1, R2, and R3, respectively. In contrast to $\mathbf{z}_r$, $\mathbf{x}_r$ is indeed zero in the time interval [0, 5] h (see Figure 8a). The extents $x_{r,1}$, $x_{r,2}$, and $x_{r,3}$ increase until reaching steady state. The profiles of $x_{r,2}$ and $x_{r,3}$ correspond to the profiles of the numbers of moles of E and G, respectively. It is very instructive to compare the profiles of the extents of reaction in different reactor types, for example $\mathbf{x}_r$ for the startup of a CSTR in Figure 8a with $\mathbf{z}_r$ for a batch reactor in Figure 3b and a semi-batch reactor in Figure 5a.

Extents of Inlet Flow. Figure 8b shows the time profiles of the extents of inlet flow $x_{in,1}$ and $x_{in,2}$ corresponding to the two inlets. The extents increase with time as soon as the corresponding inlet is activated.

Extent of Outlet Flow. Figure 8c shows the time profiles of the outflow extent x_{out}. $x_{\text{out}}(t)$ shows the fraction of the initial numbers of moles that has left the reactor at time t. It tends asymptotically to one, i.e., the initial amount of ethyl chloride has left the reactor after 48 h.

Conclusions

This article has proposed an approach for transforming the numbers of moles in open homogeneous reaction systems into extents of reaction, inlet and outlet flow. The proposed approach accounts for the effect of the nonzero initial conditions that propagate through the outlet flow, thereby generating physically meaningful extents of reaction and flow. These extents can be considered as an extension of the concept of batch extents of reaction to systems with an outlet stream; each extent of reaction represents the number of moles that is converted by the corresponding reaction and is

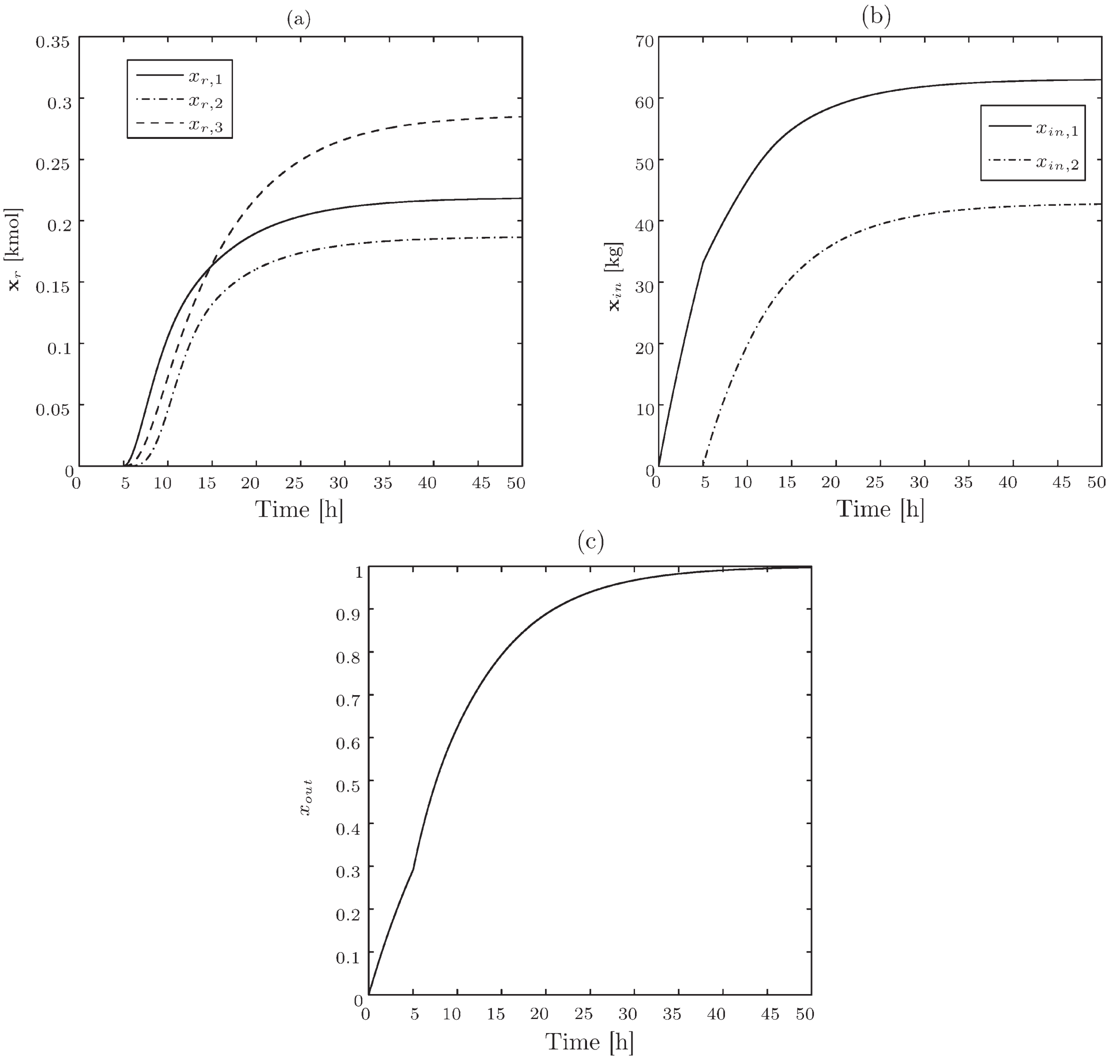

Figure 8. Various extents in the startup of CSTR.

(a) Extents of reaction $\mathbf{x}_r$, (b) extents of inlet flow $\mathbf{x}_{\text{in}}$, and (c) extent of outlet flow x_{out}.

still in the reactor, while each extent of inlet flow describes the amount of material that is added by the corresponding inlet stream and is still in the reactor. The extent of outlet flow represents the fraction of the initial number of moles that has left the reactor. Several implications such as the ability to compute the extents of reaction and flow from the measured numbers of moles have been illustrated via the simulated study of the ethanolysis of phthalyl chloride.

To put the present work in perspective, the transformations available in the literature and those proposed in this work are compared schematically in Figure 9. The transformed states exhibit widely differing characteristics. The transformed states in the literature (M2T and M3T) are mathematical reaction variants, inlet-flow variants, and invariants. In contrast, the transformed states in this work (P3T) represent physical individual extents. Future work will extend the concept of extents to heterogeneous gas–liquid reaction systems, for which mass transfer between phases needs to be considered.

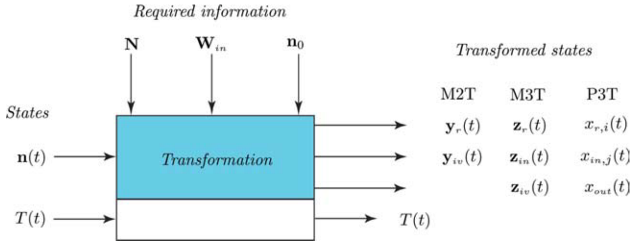

Figure 9. Comparison of the transformations available in the literature and that proposed in this work.

All the transformations are based on the stoichiometric matrix $\mathbf{N}$, and if needed also on the inlet matrix $\mathbf{W}_{\text{in}}$ and the initial conditions $\mathbf{n}_0$, to transform the numbers of moles into reaction variants and invariants. The mathematical two-way (M2T) and three-way (M3T) transformations generate transformed states that span the appropriate spaces but are denied of any physical meaning. On the other hand, the proposed physical three-way transformation (P3T) for reaction systems with inlet and outlet streams generates individual extents of reaction and flow ($i = 1,\ldots,R$ and $j = 1,\ldots,p$). Also note that all these transformations can be performed independently of the energy balance. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Acknowledgments

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Appendix A

Complete model for a homogeneous reaction system

The mole balance equations (1) hold for both gas- and liquid-phase reaction systems. The expressions for the reaction rates and the volume of the reaction mixture are described next, thus leading to a complete model suited for simulation.

Homogeneous liquid-phase reaction systems

In homogeneous liquid-phase reaction systems, $\mathbf{r}(t)$ and $V(t)$ can be expressed as follows:

$$\mathbf{r}(t)=\mathbf{r}_L(\mathbf{c}(t),T(t)),\ V(t)=\frac{m(t)}{\rho(t)}$$
$$\text{with } \mathbf{c}(t)=\frac{\mathbf{n}(t)}{V(t)},\ \rho(t)=\rho_L(\mathbf{n}(t),T(t)),$$
$$\dot{T}(t)=f_L(T(t),\mathbf{n}(t),\mathbf{u}_{\text{in}}(t),u_{\text{out}}(t),Q_{\text{ext}}(t)),\ T(0)=T_0,\ \text{(A1)}$$

where L denotes the liquid phase, $\mathbf{c}$ the S-dimensional vector of molar concentrations, T the temperature, T_0 the initial temperature, and Q_{ext} the net external heat flow due to heating, cooling, mixing, etc.

In the case of nonisothermal reaction systems, the function f_L is typically derived from an enthalpy balance. In the liquid phase, the pressure can be assumed constant and thus f_L is not an explicit function of pressure. The functions $\mathbf{r}_L$ and ρ_L are constitutive relationships that are specific to the underlying reaction system. Furthermore, $u_{\text{out}}(t)$ is often not a manipulated input but a dependent variable. For example, for a CSTR with a constant volume, the outlet mass flowrate varies with the mixture density ρ as given by Eq. 28 which reduces to $u_{\text{out}}(t) = \mathbf{1}_p^{\mathrm{T}}\ \mathbf{u}_{\text{in}}(t)$ for the constant-density case or when the reactor is at steady state.

Homogeneous gas-phase reaction systems

For homogeneous gas-phase reaction systems, four scenarios can be observed: (i) varying volume and pressure, (ii) constant volume determined by the reactor geometry and varying pressure, (iii) constant pressure by adjusting the volume, and (iv) constant volume and constant pressure, the latter being enforced by regulating the outlet flow. The scenario (ii) of constant volume and varying pressure is discussed next. The other scenarios are left to the reader. The reaction rates $\mathbf{r}(t)$ can be expressed as follows:

$$\mathbf{r}(t)=\mathbf{r}_G(\mathbf{p}(t),T(t))\ \text{with}\ \mathbf{p}(t)=\mathbf{p}_G(\mathbf{n}(t),T(t)),\mathcal{P}(t)=\mathbf{1}_S^{\mathrm{T}}\mathbf{p}(t)$$
$$\dot{T}(t)=f_G(T(t),\mathbf{n}(t),\mathcal{P}(t),\mathbf{u}_{\text{in}}(t),u_{\text{out}}(t),Q_{\text{ext}}(t)),\ T(0)=T_0,\text{(A2)}$$

where G denotes the gas phase, $\mathbf{p}$ the S-dimensional vector of partial pressures, and $\mathcal{P}$ the total pressure in the reactor. In contrast to liquid-phase reaction systems, the vector function $\mathbf{r}_G$ depends on the partial pressures $\mathbf{p}$ rather than the concentrations $\mathbf{c}$, and f_G also depends on the total pressure in the reactor. The vector function $\mathbf{p}_G$ is represented by the equation of state, e.g., the ideal gas law.

Appendix B

Proof of Theorem 1

Let the $S \times (S - R - p)$ matrix $\mathbf{Q}$, the $S \times p$ matrix $\mathbf{L}$ and the $S \times p$ matrix $\mathbf{M}$ obey the following conditions:

C1: The $S \times S$ matrix $[\mathbf{N}^{\mathrm{T}}\ \mathbf{L}\ \mathbf{Q}]$ is of rank S,

C2: The columns of $\mathbf{Q}$ are orthonormal and span the null space of $[\mathbf{N}^{\mathrm{T}}\ \mathbf{W}_{\mathrm{in}}]^{\mathrm{T}}$,

C3: The columns of $\mathbf{L}$ are orthonormal and span the null space of $[\mathbf{N}^{\mathrm{T}}\ \mathbf{Q}]^{\mathrm{T}}$,

C4: $\mathbf{M}^{\mathrm{T}}\mathbf{W}_{\mathrm{in}} = \mathbf{I}_p$, which can be achieved by choosing $\mathbf{M} = \mathbf{L}(\mathbf{W}_{\mathrm{in}}^{\mathrm{T}}\mathbf{L})^{+}$.

With $\mathbf{S}^{\mathrm{T}} = \mathbf{N}^{\mathrm{T}+}(\mathbf{I}_S - \mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}})$, the conditions C1–C4 enforce the conditions shown under the braces in Eq. 12. Applying the transformation (13) to Eq. 1 gives:

$$\begin{aligned}
\dot{\mathbf{z}}_r &= V\mathbf{r} - \frac{u_{\mathrm{out}}}{m}\,\mathbf{z}_r, & \mathbf{z}_r(0) &= \mathbf{S}^{\mathrm{T}}\mathbf{n}_0,\\
\dot{\mathbf{z}}_{\mathrm{in}} &= \mathbf{u}_{\mathrm{in}} - \frac{u_{\mathrm{out}}}{m}\,\mathbf{z}_{\mathrm{in}}, & \mathbf{z}_{\mathrm{in}}(0) &= \mathbf{M}^{\mathrm{T}}\mathbf{n}_0,\\
\dot{\mathbf{z}}_{\mathrm{iv}} &= -\frac{u_{\mathrm{out}}}{m}\,\mathbf{z}_{\mathrm{iv}}, & \mathbf{z}_{\mathrm{iv}}(0) &= \mathbf{Q}^{\mathrm{T}}\mathbf{n}_0.
\end{aligned} \tag{B1}$$

Next, Eq. 15 needs to be proven. For this, the following properties resulting from Conditions C1–C4 are used:

$$\begin{aligned}
&\mathbf{N}^{\mathrm{T}}\mathbf{N}^{+\mathrm{T}} + \mathbf{L}\mathbf{L}^{\mathrm{T}} + \mathbf{Q}\mathbf{Q}^{\mathrm{T}} = \mathbf{I}_S \text{(complementary orthonormal spaces)},\\
&\mathbf{Q}\mathbf{Q}^{\mathrm{T}}\mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}} = \mathbf{0}_{S\times S} \text{ (inlet space rotated orthogonally to}\\
&\qquad\qquad \mathbf{Q}\mathbf{Q}^{\mathrm{T}} \text{ by construction of } \mathbf{M} = \mathbf{L}(\mathbf{W}_{\mathrm{in}}^{\mathrm{T}}\mathbf{L})^{+}),\\
&\mathbf{L}\mathbf{L}^{\mathrm{T}}\mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}} = \mathbf{L}\mathbf{L}^{\mathrm{T}} \text{ (equivalent spaces)}.
\end{aligned} \tag{B2}$$

Premultiplying both sides of Eq. 13 with $[\mathbf{N}^{\mathrm{T}}\ \mathbf{W}_{\mathrm{in}}\ \mathbf{Q}]$ gives:

$$\begin{aligned}
\mathbf{N}^{\mathrm{T}}\mathbf{z}_r + \mathbf{W}_{\mathrm{in}}\mathbf{z}_{\mathrm{in}} + \mathbf{Q}\mathbf{z}_{\mathrm{iv}} &= (\mathbf{N}^{\mathrm{T}}\mathbf{S}^{\mathrm{T}} + \mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}} + \mathbf{Q}\mathbf{Q}^{\mathrm{T}})\,\mathbf{n}\\
&= (\mathbf{N}^{\mathrm{T}}\mathbf{N}^{\mathrm{T}+}\,(\mathbf{I}_S - \mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}}) + \mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}} + \mathbf{Q}\mathbf{Q}^{\mathrm{T}})\,\mathbf{n}\\
&= (\mathbf{N}^{\mathrm{T}}\mathbf{N}^{\mathrm{T}+} + (\mathbf{L}\mathbf{L}^{\mathrm{T}} + \mathbf{Q}\mathbf{Q}^{\mathrm{T}})\mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}} + \mathbf{Q}\mathbf{Q}^{\mathrm{T}})\,\mathbf{n}\\
&= (\mathbf{N}^{\mathrm{T}}\mathbf{N}^{\mathrm{T}+} + \mathbf{L}\mathbf{L}^{\mathrm{T}} + \mathbf{Q}\mathbf{Q}^{\mathrm{T}})\,\mathbf{n} = \mathbf{n}\\
\Longleftrightarrow \mathbf{n} &= \mathbf{N}^{\mathrm{T}}\mathbf{z}_r + \mathbf{W}_{\mathrm{in}}\,\mathbf{z}_{\mathrm{in}} + \mathbf{Q}\mathbf{z}_{\mathrm{iv}}.
\end{aligned} \tag{B3}$$

An algorithm for computing the matrices $\mathbf{S}$, $\mathbf{M}$, and $\mathbf{Q}$ is given in Appendix D.

Appendix C

Proof of Theorem 2

The proof has three parts. In the first part of the proof, it is shown that $\mathbf{1}_{(S-R-p)}^{\mathrm{T}}\ \mathbf{Q}^{\mathrm{T}}\mathbf{n}_0 \neq 0$ is guaranteed through the working assumption $\mathrm{rank}([\mathbf{N}^{\mathrm{T}}\ \mathbf{W}_{\mathrm{in}}\ \mathbf{n}_0]) = R + p + 1$. This assumption indicates that $\mathbf{n}_0$ does not belong to the column space of $[\mathbf{N}^{\mathrm{T}}\ \mathbf{W}_{\mathrm{in}}]$, which, with Condition C2, is equivalent to saying that $\mathbf{n}_0$ does not belong to the null space of $\mathbf{Q}^{\mathrm{T}}$. Hence, $\mathbf{Q}^{\mathrm{T}}\ \mathbf{n}_0 \neq \mathbf{0}_{\mathrm{S-R-p}}$. As $\mathbf{Q}$ is of full rank $(S - R - p)$, $\mathbf{1}_{(S-R-p)}^{\mathrm{T}}\ \mathbf{Q}^{\mathrm{T}} \neq \mathbf{0}_S$ and $\mathbf{1}_{(S-R-p)}^{\mathrm{T}}\ \mathbf{Q}^{\mathrm{T}}\ \mathbf{n}_0 \neq 0$ follow.

In the second part of the proof, Eqs. 20 and 23 are derived. For this, the following properties resulting from Conditions C1–C4 are used: $\mathbf{q}_0^{\mathrm{T}}\mathbf{N}^{\mathrm{T}} = \mathbf{0}_R^{\mathrm{T}}$, $\mathbf{q}_0^{\mathrm{T}}\mathbf{W}_{\mathrm{in}} = \mathbf{0}_p^{\mathrm{T}}$, and $\mathbf{q}_0^{\mathrm{T}}\ \mathbf{n}_0 = 1$. Applying the transformation (18) and

$$\mathbf{x}_{\mathrm{iv}} = \mathbf{Q}_0^{\mathrm{T}}\mathbf{n} \quad \text{with} \quad \mathbf{Q}_0^{\mathrm{T}} = \mathbf{Q}^{\mathrm{T}}(\mathbf{I}_S - \mathbf{n}_0\,\mathbf{q}_0^{\mathrm{T}}) \tag{C1}$$

to Eq. 1 gives:

$$\begin{aligned}
\dot{\mathbf{x}}_r &= V\,\mathbf{r} - \frac{u_{\mathrm{out}}}{m}\mathbf{x}_r, & \mathbf{x}_r(0) &= \mathbf{0}_R,\\
\dot{\mathbf{x}}_{\mathrm{in}} &= \mathbf{u}_{\mathrm{in}} - \frac{u_{\mathrm{out}}}{m}\mathbf{x}_{\mathrm{in}}, & \mathbf{x}_{\mathrm{in}}(0) &= \mathbf{0}_p,\\
\dot{\lambda} &= -\frac{u_{\mathrm{out}}}{m}\,\lambda, & \lambda(0) &= 1,\\
\dot{\mathbf{x}}_{\mathrm{iv}} &= -\frac{u_{\mathrm{out}}}{m}\mathbf{x}_{\mathrm{iv}}, & \mathbf{x}_{\mathrm{iv}}(0) &= \mathbf{0}_{S-R-p}.
\end{aligned} \tag{C2}$$

As $\mathbf{x}_{\mathrm{iv}}(0) = \mathbf{0}_{S-R-p}$, $\mathbf{x}_{\mathrm{iv}}(t) = \mathbf{0}_{S-R-p}$ for all time t. Hence, $\mathbf{x}_{\mathrm{iv}}$ can be dropped from Eq. C2.

In the last part of the proof, Eq. 21 is derived. For this, the following properties are used: (i) Eq. B2, (ii) $\mathbf{Q}\mathbf{x}_{\mathrm{iv}}(t) = \mathbf{0}_S$ as $\mathbf{x}_{\mathrm{iv}}(t) = \mathbf{0}_{S-R-p}$, and (iii) $(\mathbf{N}^{\mathrm{T}}\mathbf{S}^{\mathrm{T}} + \mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}} + \mathbf{Q}\mathbf{Q}^{\mathrm{T}}) = \mathbf{I}_S$ from Eq. B3. Premultiplying both sides of Eq. 18 with $[\mathbf{N}^{\mathrm{T}}\ \mathbf{W}_{\mathrm{in}}\ \mathbf{n}_0]$ leads to:

$$\begin{aligned}
\mathbf{N}^{\mathrm{T}}\mathbf{x}_r + \mathbf{W}_{\mathrm{in}}\mathbf{x}_{\mathrm{in}} + \lambda\mathbf{n}_0 &= \mathbf{N}^{\mathrm{T}}\mathbf{x}_r + \mathbf{W}_{\mathrm{in}}\mathbf{x}_{\mathrm{in}} + \lambda\mathbf{n}_0 + \mathbf{Q}\mathbf{x}_{\mathrm{iv}}\\
&= (\mathbf{N}^{\mathrm{T}}\mathbf{S}^{\mathrm{T}} + \mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}} + \mathbf{Q}\mathbf{Q}^{\mathrm{T}})(\mathbf{I}_S - \mathbf{n}_0\,\mathbf{q}_0^{\mathrm{T}})\,\mathbf{n} + \mathbf{n}_0\mathbf{q}_0^{\mathrm{T}}\mathbf{n}\\
&= (\mathbf{I}_S - \mathbf{n}_0\,\mathbf{q}_0^{\mathrm{T}})\,\mathbf{n} + \mathbf{n}_0\mathbf{q}_0^{\mathrm{T}}\mathbf{n} = \mathbf{n}\\
\Longleftrightarrow \mathbf{n}(t) &= \mathbf{N}^{\mathrm{T}}\mathbf{x}_r(t) + \mathbf{W}_{\mathrm{in}}\mathbf{x}_{\mathrm{in}}(t) + \mathbf{n}_0\,\lambda(t).
\end{aligned} \tag{C3}$$

Appendix D

Algorithm to compute S, M, and Q

The algorithm assumes $\mathrm{rank}([\mathbf{N}^{\mathrm{T}}\ \mathbf{W}_{\mathrm{in}}]) = R + p$, although it can easily be extended to the case of $\mathrm{rank}([\mathbf{N}^{\mathrm{T}}\ \mathbf{W}_{\mathrm{in}}]) < R + p$. The objective is to compute the matrices $\mathbf{Q}$, $\mathbf{L}$, $\mathbf{M}$, and $\mathbf{S}$ that fulfill the conditions C1–C4 given in Appendix B.

1. Apply the singular value decomposition (SVD) to the matrix $[\mathbf{N}^{\mathrm{T}}\ \mathbf{W}_{\mathrm{in}}]$:

$$[\mathbf{N}^{\mathrm{T}}\ \ \mathbf{W}_{\mathrm{in}}] = \mathbf{U}_1\mathbf{S}_1\mathbf{V}_1^{\mathrm{T}}.$$

Let $\mathbf{U}_1 = [\mathbf{U}_{1,1}\ \mathbf{U}_{1,2}]$, where $\mathbf{U}_{1,1}$ and $\mathbf{U}_{1,2}$ are of dimension $S \times (R + p)$ and $S \times (S - R - p)$, respectively. Then, $\mathbf{Q} = \mathbf{U}_{1,2}$.

2. Note that $\mathrm{rank}([\mathbf{N}^{\mathrm{T}}\ \mathbf{Q}]) = S - p$. Apply SVD to the matrix $[\mathbf{N}^{\mathrm{T}}\mathbf{Q}]$:

$$[\mathbf{N}^{\mathrm{T}}\ \ \mathbf{Q}] = \mathbf{U}_2\mathbf{S}_2\mathbf{V}_2^{\mathrm{T}}.$$

Let $\mathbf{U}_2 = [\mathbf{U}_{2,1}\ \mathbf{U}_{2,2}]$, where $\mathbf{U}_{2,1}$ and $\mathbf{U}_{2,2}$ are of dimension $S \times (S - p)$ and $S \times p$, respectively. Then, $\mathbf{L} = \mathbf{U}_{2,2}$.

3. Compute $\mathbf{M} = \mathbf{L}(\mathbf{W}_{\mathrm{in}}^{\mathrm{T}}\mathbf{L})^{+}$.

4. Compute $\mathbf{S}^{\mathrm{T}} = \mathbf{N}^{\mathrm{T}+}(\mathbf{I}_S - \mathbf{W}_{\mathrm{in}}\mathbf{M}^{\mathrm{T}})$.

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