

Extents of Reaction and Mass Transfer in the Analysis of Chemical Reaction Systems

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॥ श्री गणेशाय नमः ॥

विद्या ददाति विनयं विनयाद्याति पात्रतां ।

पात्रत्वाद्धनमाप्नोति धनाद्धर्मं ततः सुखं ॥

–हितोपदेश, १२ शतक

Knowledge gives humility, from humility comes worthiness, from worthiness one gets
wealth, from wealth (one does) righteous deeds, from that (comes) joy.

Hitopadesha, 12th CE

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Abstract

Monitoring, control and optimization of chemical reaction systems often requires in-depth analysis of the underlying reaction mechanisms. This dissertation investigates appropriate tools that facilitate the analysis of homogeneous and gas-liquid reaction systems. The main contribution is a novel procedure for computing the *extents of reaction* and the *extents of mass transfer* for reaction systems with inlet and outlet streams. These concepts can help reduce the dimension of reaction models and are useful in the identification of reaction kinetics based on concentrations and spectral data.

Extents of reaction, mass transfer and flow

The concept of extents of reaction is well established for single-phase closed systems such as batch homogeneous reactors. However, it is difficult to compute the extent of reaction for open and heterogeneous reactors due to material exchange with the surroundings via inlet and outlet streams and between phases via mass transfer.

For open homogeneous reaction systems involving S species, R independent reactions, p independent inlet streams and one outlet stream, this dissertation proposes a *linear transformation* of the number of moles vector (S states) into four distinct parts, namely, the extents of reaction, the extents of inlet, the extent of outlet and the invariants, using only the stoichiometry, the inlet composition and the initial conditions.

The open gas-liquid reaction systems considered in this thesis involve S_g species, p_g independent inlets and one outlet in the gas phase, S_l species, R independent reactions, p_l independent inlets and one outlet in the liquid phase. In addition, there are p_m mass-transfer fluxes between the two phases. For these systems, various extents are developed successively for the liquid and gas phases. Using only the stoichiometry, the inlet composition, the initial conditions, and knowledge of the species transferring between phases, a linear transformation of the numbers of moles (S_l states) in the liquid into five distinct parts is proposed, namely, the extents of reaction, the extents of mass transfer, the extents of liquid inlet, the extent of liquid outlet and the invariants. Similarly, a transformation of the numbers of moles (S_g states) in the gas phase into four distinct parts is proposed to generate the extents of mass transfer, the extents of gas inlet, the extent of gas outlet and the invariants.

Minimal state representation and state reconstruction

A state representation is minimal if (i) it can be transformed into variant states that evolve with time and invariants that are constant with time (representation condition), and (ii) the transformed model is minimal (minimality condition).

Since the linear transformation transforms the numbers of moles into variant states (the extents) and invariant states, it satisfies the representation condition. For homogeneous reaction systems, the linearly transformed model is of the order $(R + p + 1)$, while the order of the linearly transformed model for open gas-liquid reaction systems

is $(R + p_l + p_g + 2p_m + 2)$. Using the concept of accessibility of nonlinear systems, the conditions under which the transformed models are minimal state representations are derived for both types of reaction systems.

Since it is often not possible in practice to measure the concentrations of all the species, the unmeasured concentrations have to be reconstructed from available measurements. Using the measured flowrates and the proposed transformations, it is possible to reconstruct the unmeasured concentrations without knowledge of the reaction and mass-transfer rate expressions. Furthermore, it is shown that the minimal number of measured concentrations is R for homogeneous reactors and $(R + p_m)$ for gas-liquid reactors.

Use of concentrations and spectral data

The identification of reaction kinetics can be done incrementally or globally from experimental data. Using measured concentrations and spectral data with knowledge of pure-component spectra, incremental identification proceeds in two steps: (i) computation of the extents of reaction and mass transfer from measured data, and (ii) estimation of the parameters of the *individual* reaction and mass-transfer rates from the computed extents.

In the first step, the linear transformation is applied to compute the extents of reaction, mass transfer and flow directly from measured concentrations without knowledge of the reaction and mass-transfer rate expressions. The transformation can be extended to measured spectral data, provided the pure-component spectra are known. An approach is developed for the case where concentrations are only available for a subset of the reacting species. In the second step, the unknown rates can be identified individually for each reaction or each mass transfer from the corresponding individual extent using the *integral method*. For the case of measured concentrations corrupted with zero-mean Gaussian noise, it is shown that the transformation gives unbiased estimates of the extents.

For the case of spectral data with unknown pure-component spectra, the contributions of the reactions and mass transfers can be computed by removing the contributions of the inlet flows and the initial conditions. This leads to the reaction- and mass-transfer-variant (RMV) form of spectral data, from which the reaction and mass-transfer rate parameters can be estimated simultaneously. However, if the RMV-form is rank deficient, the rank must be augmented before applying factor-analytical methods. In such cases, it is shown that, for example, gas consumption data can be used for rank augmentation.

The concepts and tools are illustrated using simulated data. Several special reactors such as batch, semi-batch and continuous stirred-tank reactors are considered.

Key words:

Extents of reaction; Extents of mass transfer; Minimal state representation; Identification; Reaction kinetics; Transport phenomena; Homogeneous reactors; Gas-liquid reactors.

Résumé

Le suivi, la commande, et l'optimisation des systèmes réactionnels chimiques nécessitent généralement une analyse approfondie des mécanismes réactionnels sous-jacents. Cette dissertation traite du développement d'outils appropriés, qui facilitent l'analyse des systèmes réactionnels homogènes et gaz-liquide. La contribution principale réside dans le développement d'une procédure nouvelle, pour le calcul des *avancements des réactions* et des *avancements des transferts de masse* pour les réacteurs continus. Ces concepts peuvent aider à réduire la dimension des modèles réactionnels et sont utiles pour l'identification des cinétiques réactionnelles sur la base de mesures de concentrations et de mesures spectrales.

Avancements des réactions, transfert de masse, et débit entrée

Le concept d'avancement de réaction est bien établi pour les systèmes fermés, par exemple pour les réacteurs fermés uniformes. Cependant, il est difficile d'étendre ces concepts aux réacteurs continus et/ou hétérogènes, à cause des échanges de matière avec l'environnement - à travers débits d'entrée et de sortie - et entre les phases, par transfert de masse.

Pour des systèmes réactionnels homogènes impliquant S espèces, R réactions indépendantes, p entrées indépendantes, et une sortie, cette dissertation propose une transformation linéaire du vecteur composé du nombre de moles en quatre parties distinctes: (1) les advancements de réaction, (2) les advancements d'entrée, (3) les advancements de sortie, et (4) les invariants, en utilisant seulement la stœchiométrie, la composition de l'alimentation, et les condition initiales.

Les systèmes réactionnels gaz-liquide considérés impliquent S_g espèces, p_g entrées indépendantes, et une sortie gazeuse, S_l espèces, R réactions indépendantes, p_l entrées indépendantes, et une sortie liquide. De plus, p_m flux de transfert de masse entre les deux phases sont considérés. Pour ces systèmes, le concept des différents advancements est développé successivement pour les phases liquide et gazeuse. Une transformation linéaire du vecteur composé du nombre de moles (S_l états) dans la phase liquide en cinq parties est proposée, pour obtenir: (1) les advancements des réactions, (2) les advancements des transferts de masse, (3) les advancements d'entrée liquide, (4) l'avancement de sortie, et (5) les invariants. Cette transformation nécessite de l'information concernant la stœchiométrie, la composition d'alimentation, les conditions initiales, et les espèces qui sont transférées à l'interface entre les deux phases. De façon similaire, une transformation du vecteur composé du nombre de moles (S_g états) dans la phase gazeuse en quatre parties est proposée, pour obtenir: (1) les advancements des transferts de masse, (2) les advancements des alimentations gaz, (3) l'avancement de sortie, et (4) les invariants.

Représentation d'état minimale et reconstruction d'état

Une représentation d'état est dite minimale si (i) on peut trouver une transformation qui permet de séparer les états variant avec le temps des états constants (condition de représentation), et (ii) le modèle transformé est minimal (condition de minimalité).

Comme les transformations linéaires discutées ci-dessus séparent les états constants des états variant avec le temps, elles vérifient par construction la condition de représentation (i). Pour les systèmes réactionnels homogènes, le modèle linéairement transformé est d'ordre $(R + p + 1)$. De la même façon, l'ordre des modèle linéairement transformés est $(R + p_l + p_g + 2p_m + 2)$ pour le cas des réacteurs hétérogènes. Les conditions pour lesquelles les modèles transformés vérifient la condition de minimalité (ii) sont établies en utilisant le concept d'accessibilité des systèmes nonlinéaires.

Puisqu'il n'est pas souvent possible de mesurer les concentrations de toutes les espèces, il est nécessaire de reconstruire les concentrations non mesurées à partir des mesures disponibles. De plus, les cinétiques réactionnelles et les transferts de masse sont souvent inconnus. Les transformations développées séparent les contributions des réactions, des transferts de masse, des entrées, et de la sortie. Cette séparation effectuée, on propose une approche de reconstruction des concentrations non mesurées en utilisant les débits d'alimentation et les transformations. De plus, on démontre que le nombre de concentrations minimales nécessaires est R pour les réacteurs homogènes et $(R + p_m)$ pour les réacteurs gaz-liquide.

Utilisation des mesures de concentration et spectrales

Il est possible d'identifier les cinétiques réactionnelles incrémentalement (et individuellement) ou globalement (et simultanément) à partir de données expérimentales. En utilisant des mesures de concentration et spectrales avec les informations des spectres des composants purs, l'identification incrémentale peut être réalisée en deux étapes: (i) le calcul des avancements des réactions et des transferts de masse sur la base des mesures, et (ii) l'estimation des paramètres des vitesses des réactions et des transferts de masse sur la base des avancements ainsi calculés.

Pendant (i), la transformation linéaire est appliquée sans il soit nécessaire d'utiliser des informations sur les expressions des vitesses des réaction et des transferts de masse. On développe également une approche pour le cas spécial dans lequel les concentrations ne sont disponibles que pour une partie des espèces considérées. La transformation linéaire est aussi appliquée à des données spectrales si les spectres des composants purs sont connus. Ensuite, il est possible d'identifier les vitesses inconnus pour chaque réaction ou chaque transfert de masse, à partir de l'avancement individuel correspondant, par la *méthode intégrale*. Pour le cas des concentrations corrompues par du bruit Gaussien de moyenne nulle, on démontre que la transformation donne des estimations des avancements sans biais.

Quand les spectres des composants purs sont inconnus, on calcule les contributions des réactions et des transferts de masse en retirant les contributions des débits d'entrée et des conditions initiales. Cette nouvelle forme de données spectrales (forme RMV) permet d'estimer simultanément les paramètres des vitesses des réactions et des transferts de masse. Cependant, si la forme-RMV est de rang déficient, on doit augmenter ce rang avant d'appliquer les méthodes du type "factor analysis" (FA). Dans de tels cas, on

démontre que les données de consommation du gaz peuvent être utilisées pour effectuer cette augmentation du rang.

Les différents concepts, les outils développés et leur mise en œuvre sont illustrés en simulation. Plusieurs réacteurs, tels que des réacteurs fermés uniformes, semi-fermés uniformes, et aussi des réacteurs parfaitement agités continus sont considérés.

Mots-clés:

Avancements de réaction; Avancements de transfert de masse; Représentation d'état minimale; Identification; Lois cinétiques; Phénomène de transfert; Réacteurs homogènes; Réacteurs gaz-liquide.

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Nomenclature

Accents

$\bar{(\cdot)}$	extended inlets
(\cdot)	quantities corresponding to mass transfers in the gas phase
$\hat{(\cdot)}$	computed or estimated quantities
$\dot{(\cdot)}$	continuous approximation of discrete low-resolution measurements in Chapters 5 and 6

Calligraphic symbols

\mathcal{P}	vector of partial pressure (S -dim.)
\mathcal{O}	set
\mathcal{N}	Gaussian distribution
\mathcal{N}_l	matrix of numbers of moles ($H \times S_l$)
\mathcal{P}	pressure or partial pressure
\mathcal{P}_t	total pressure
\mathcal{S}	set of species
\mathcal{U}	set of vector-valued function (v -dim.)
\mathcal{W}	weighting matrix ($H \times H$)
$\mathcal{W}(t)$	solution of Eq. (4.1) at time t

Greek symbols

β	random vector
Σ_c	matrix of measurement noise ($S \times S$)
δ_m	vector of variables expressing the difference between the extents of mass transfer in the gas and liquid phases (p_m -dim.)
η	non-zero arbitrary real constant
λ	outlet variant or discounting variable
μ	mean
ν	stoichiometric coefficient

ω_m	vector of gas consumption data (H -dim.)
ρ	density
σ	standard deviation
θ_m	rate parameter vector (q -dim.)
θ_r	rate parameter vector (l -dim.)
v	the number of inputs in Eq. (4.1)
Λ_l	vector of discounting variable (H -dim.)
Ω_m	matrix of gas consumption data ($H \times p_m$)
ξ	batch extent of reaction or molar mass-transfer flux
$\xi_{m,j}$	overall extent of the j th mass transfer
$\xi_{r,i}$	overall extent of the i th reaction
ξ	vector of extents of reaction (R -dim.)
ξ_1	vector of variant states in Eq. (4.3) (q -dim.)
ξ_2	vector of invariant states in Eq. (4.4) ($(S - q)$ -dim.)
ζ	mass-transfer rate
ζ	mass-transfer vector (p_m -dim.)

Operators

$(\cdot)^+$	Moore-Penrose pseudo-inverse of (\cdot)
$(\cdot)_i$	i th row of (\cdot)
$\Delta(\cdot)$	accessibility distribution of (\cdot)
$\text{diag}(\cdot)$	diagonalize (\cdot)
$E[\cdot]$	expectation of $[\cdot]$
$\nabla(\cdot)$	spatial derivative of (\cdot)
$\text{rank}(\cdot)$	rank of (\cdot)
$\text{var}[\cdot]$	variance of $[\cdot]$
$F(\cdot), g(\cdot)$	function of (\cdot)
$O(\cdot)$	order of magnitude (\cdot)

Roman symbols

A	measured spectra matrix ($H \times L$)
a	measured spectral vector for L channels (L -dim.)
a₀	vector of initial spectrum (L -dim.)
A_{in}	matrix of liquid-inlet spectra ($p_m \times L$)
A_m	matrix of mass-transfer spectra ($p_m \times L$)
A_v	volume-weighted spectral matrix ($H \times L$)
a_v	volume-weighted spectral vector (L -dim.)
N_e	extended stoichiometric matrix ($\bar{S}_a \times (R + p_m)$)
c	vector of measured concentrations (S -dim.)
w^k	vector of weight fractions of the k th inlet stream (S -dim.)
W_{in}	inlet weight-fraction matrix ($S \times p$)
d	contribution of reactions to the numbers of moles produced or consumed by the reactions in (S -dim.)

E	pure-component spectra matrix ($S_l \times L$)
e	vector of measurement noise (S -dim.)
f, g	vector fields
f^r	vector of reaction fluxes (S -dim.)
f^t	vector of reaction and mass-transfer fluxes ($(S_l + S_g)$ -dim.)
$\hat{\mathbf{x}}_{m,l,j}$	computed extent of the j th mass transfer (H -dim.)
$\hat{\mathbf{x}}_{r,i}$	computed extent of the i th reaction (H -dim.)
H_{rm}	spectral matrix in RMV-form ($H \times L$)
J	Jacobian matrix in Chapter 4
M	projection matrix ($S \times p$)
M₀	projection matrix in the linear transformation ($S \times p$)
M_w	pure component molecular weight matrix ($S \times S$)
N	stoichiometric matrix ($R \times S$)
n	vector of number of moles (S -dim.)
n₀	vector of initial numbers of moles (S -dim.)
N_{l,a,e}	extended stoichiometric matrix ($S_{l,a} \times (R + p_{m_l})$)
1	vector of appropriate dimension with all elements being 1
P	null space of N ($S \times (S - R)$)
Q	projection matrix ($S \times (S - R - p)$)
q	row of Q (S -dim.)
Q₀	projection matrix in the linear transformation ($S \times (S - R - p)$)
q₀	projection vector in the linear transformation (S -dim.)
q_{in}	vector of inlet volumetric flowrates (p -dim.)
r	vector of reaction rates (R -dim.)
S	projection matrix ($S \times R$)
S₀	projection in the linear transformation ($S \times R$)
u_{in}	vector of inlet mass flowrates (p -dim.)
V_l	$= \text{diag}(V_l(t_0), V_l(t_1), \dots, V_l(t_h))$, diagonal matrix of V_l ($H \times H$)
W	molecular weight matrix ($S \times p$)
w	state vector in Eq. (4.1)
W_{in}	inlet-composition matrix ($S \times p$)
W_{m,f}	mass-transfer matrix for the f phase ($S_f \times p_m$)
x	vector of the extents or variants
X_{in}	matrix of extents of inlet ($H \times p_l$)
X_r	matrix of extents of reaction ($H \times R$)
X_{m,l}	matrix of extents of mass transfer ($H \times p_m$)
X_{rm}	matrix of extents of reaction and mass transfer ($H \times R + p_m$)
y	state vector in two-way decomposition
z	state vector in three-way decomposition
A	specific interfacial area
f	function in Section 3.1.1
h	time instant, $h = 0, 1, \dots, H$
H_c	Henry constant
k_i	rate constant of the i th reaction
k_j	mass transfer coefficient of the j th mass transfer

K_o	overall mass transfer coefficient
m	mass of reaction mixture
p	number of independent inlets
p_a	the number of absorbing transferring species
q	minimal order
q_{out}	outlet volumetric flowrate
R	number of independent reactions
R_s	number of slow reactions
S	number of species
t	time
u_{out}	outlet mass flowrate
V_t	total reactor volume
y	mole fraction in the gas bulk
J	objective function

Subscripts

a	related to S_a available species
c	related to measurement noise
f	related to f phase
g	related to the gas phase
gl	transferring from the gas to the liquid
i	running index for the reactions
in	related to inlet streams
iv	related to invariants
j	running index for the mass transfers
k	running index for the inlets
l	related to the liquid phase
lg	transferring from the liquid to the gas
m	related to the mass transfers
m_g	related to the extents of mass transfer computed from the gas phase
m_l	related to the extents of mass transfer computed from the liquid phase
na	related to non-reacting but absorbing reacting species
out	related to outlet streams
r	related to reactions
ra	related to absorbing reacting species
rn	related to non-absorbing reacting species
s	running index for the species
u	related to S_u unavailable species
rm	related to reaction and mass-transfer contributions

Superscripts

aug	related to augmented quantities
f	related to fast reaction

g	related to the gas phase
L	lower bound in Sections 5.4 and 5.3
l	related to the liquid phase
r	related to reaction fluxes
rm	related to reaction and mass-transfer fluxes
s	related to slow reaction
t	related to reaction and mass-transfer fluxes in the liquid and gas phases
U	upper bound in Sections 5.4 and 5.3

Chapter 1

Introduction

1.1 Motivation

Chemical reactions are present in various spheres of our lives. They occur in many fields such as in basic science, chemistry and biology, and in applied science, chemical engineering and biotechnology. A large number of industrial processes in chemical engineering and biotechnology depend on (bio-)chemical reactions to convert raw materials into desired products that include polymers, organic chemicals, vitamins, vaccines and drugs. This dissertation deals with the chemical reactions taking place in the latter fields, i.e. chemical and biotechnological industries.

In the wake of rapidly changing market conditions and stringent environmental specifications, chemical and biotechnological industries need to invent and implement new processes in a short time to remain competitive. Consequently, one important goal of these industries is rapid process development with flexibility and selectivity in production, including quality control, safety and environmental protection. Chemical reaction systems are essential parts of industrial processes and involve *chemical reactions*, material exchange via inlets, outlets and mass transfer, and energy exchange via heating and cooling. Reliable process models are used to minimize the production of undesirable products and pollutants, increase efficiency, and improve quality through model-based monitoring, control, and optimization.

Process models of chemical reaction systems are typically first-principles models that describe the state evolution (the concentrations, the temperature, the volume) by means of conservation equations of differential nature (molar balances, heat balances, continuity equation) and constitutive equations of algebraic nature (e.g. equilibrium relationships and rate expressions). They usually include information regarding the underlying reactions (e.g. stoichiometries, heats of reaction, reaction kinetics), the mass transfers between phases, and the operational mode of the reactor (e.g. the initial conditions, external exchange terms, operational constraints). A reliable description of reaction kinetics and transport processes (such as mass transfer) poses the main challenge in building first-principles models for chemical reaction systems.

In practice, a reliable description of these phenomena is constructed from experimental data obtained in the laboratory or collected during production as shown in Figure 1.1. A kinetic model used in production is typically developed in two steps as

shown in Figure 1.1. Process development in the laboratory is the first step, in which experimental data are explored and features such as the time instants of the start/stop of the main and side reactions, the presence or absence of accumulation of specific species, and safety parameters are extracted. These features can be summarized in a feature-based descriptive model. When process development is performed in the laboratory, it is possible to influence and measure many variables in planned experiments under controlled experimental conditions.

During process development in the laboratory, common on-line measurements such as temperature, pressure, inlet and outlet mass flowrates, and off-line measurements such as the concentrations of the main and side products at batch end are routinely available. In addition to these measurements, advanced instruments such as calorimeters and spectrometers (mid-infrared MIR; near-infrared NIR; ultraviolet/visible - UV/VIS) enable the indirect measurement of key variables such as the heat flow and the concentrations of initial and final products in-situ or at-line.

For the purpose of model-based monitoring, control and optimization, the kinetic model obtained at the process development stage needs to be adjusted to the production environment. This adjustment is typically done with only a few measurements and a restricted choice of production conditions due to safety and production constraints. Hence, it is of interest to be able to solve the following problems to meet industrial goals based on the experimental data and prior knowledge regarding the reaction systems:

- (P1) Build first-principles models,
- (P2) Simplify dynamic reaction models to a form that brings out the key features,
- (P3) Monitor, control and optimize reaction systems.

Problem P1 deals with the development of mathematical models that describe the dynamic behavior of reaction systems. The solutions to Problems P1 and P2 help perform computer simulations under various scenarios and reduce cost and time in the laboratory. Consequently, they speed up process development and also help move the developed process from the laboratory to production. The solution to P3 helps improve product quality, safety and environmental protection in production. The solutions to Problems P1 and P2 also help develop effective methods to solve Problem P3. Hence, the solutions to Problems P1–P3 call for systematic approaches based on mathematical modeling and analysis of chemical reaction systems.

To meet these challenges and deal with Problems P1–P3, this dissertation develops a methodology based on system-theoretical and data analysis of chemical reaction systems, in particular for homogeneous and gas-liquid reaction systems.

Building first-principles models

Building first-principles models of reaction systems through the identification of kinetic models is an essential task during the process development stage. The identification of a kinetic model involves the determination of a model structure (reaction stoichiometry, reaction-rate expressions, mass-transfer-rate expressions) and of the corresponding

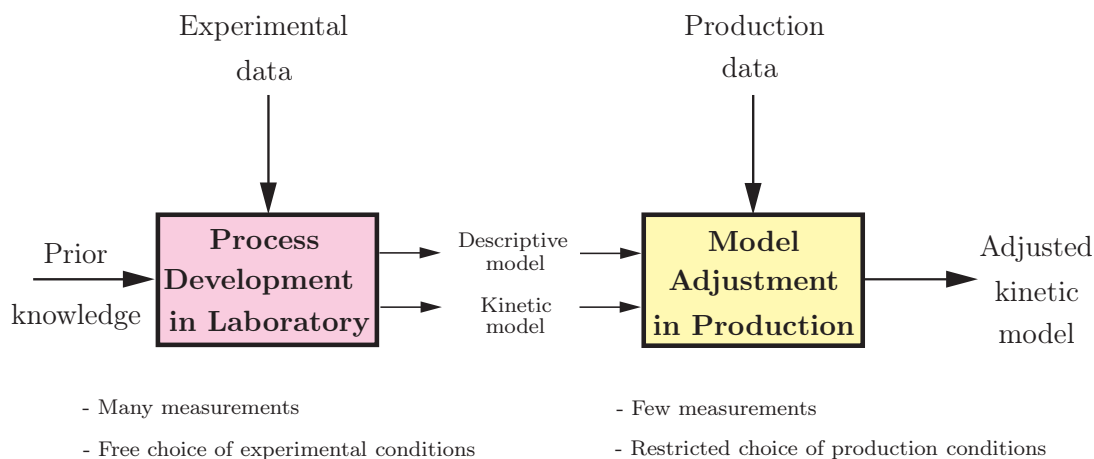


Figure 1.1 Schematic diagram illustrating the development of a kinetic model at the process development stage in the laboratory and its adaptation in production.

parameters. In this dissertation, ‘kinetic model’ will be used for a model that includes reaction stoichiometry, reaction rates, and possibly mass-transfer rates. In practice, the kinetic model of a given reaction system must be identified from measurements. In the literature, the reaction stoichiometry and the expressions for the reactions and the mass transfers are identified simultaneously by solving an optimization problem for the rate parameters. On the other hand, it could help to break down the identification of a kinetic model into two steps: (i) compute the extents of reaction and mass transfer from measured data without knowledge of the reaction-rate and mass-transfer-rate expressions, and (ii) identify each rate expression individually from the corresponding extent of reaction or mass transfer.

Postulate

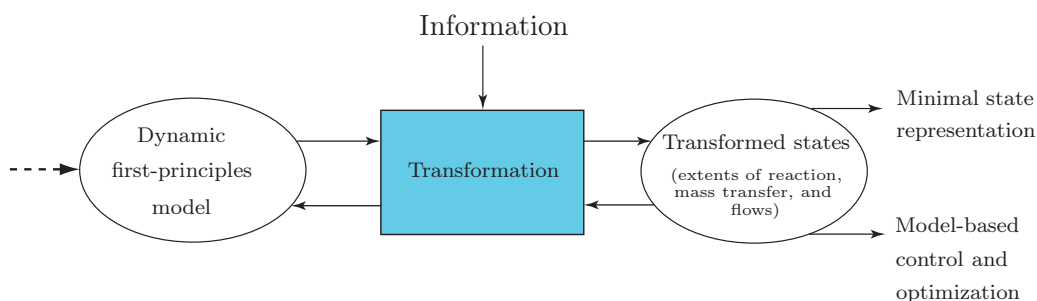
The concept of extents of reaction and mass transfer helps to describe the behavior of chemical reaction systems. Such a concept is useful from both a system-theoretical and a data-analysis view point. The following postulate can be formulated:

The number of moles vector of a reaction system can be transformed to the extents of reaction, mass transfer and flow, which helps solve Problems P1–P3 in two ways: Firstly, the transformation can help build the dynamic model from various measurements such as concentrations and spectral data; secondly, if a dynamic reaction model is available, the transformation can be used to simplify the model.

This postulate, which will be investigated in this dissertation, can be divided into two parts as shown in Figure 1.2. In the first part, a transformation of the dynamic reaction model to the extents of reaction, mass transfer and flow will be developed

without knowledge of the reaction-rate and mass-transfer-rate expressions. Information regarding the reaction stoichiometry, the inlet compositions, the species transferring between phases, and the initial conditions will be used to develop the transformation. A system-theoretical analysis of the transformed states will lead to minimal state representation and minimal information for state reconstruction. In the second part, the transformation will be used in the analysis of concentrations and spectral data. Data analysis will lead to a novel incremental method for the identification of kinetic models that can be useful for process monitoring, control and optimization of reaction systems.

System-theoretical analysis (Chapters 2–4)



Data analysis (Chapter 5)

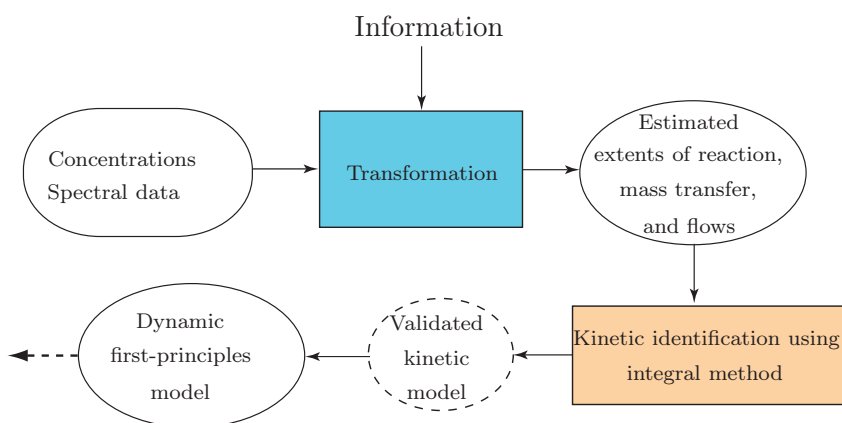


Figure 1.2 Schematic diagram illustrating the two-part postulate in this dissertation: system-theoretical analysis, and data analysis.

1.2 State of the art

1.2.1 Reaction variants, flow variants and invariants

In the study of reaction systems, it is important to distinguish between the states that evolve with reaction progress, labeled *reaction variants*, and the states that do not, labeled *reaction invariants*. The numbers of moles has been broken down into reaction variants and invariants in the literature [6, 31]. As expected, the reaction invariants are independent of the reactions; however, the reactions variants do not only represent the contribution of the reactions since they are also affected by inlet streams [6, 31, 96]. Srinivasan et al. [75] proposed a nonlinear transformation of the numbers of moles into reaction variants, flow variants, and reaction and flow invariants. The proposed nonlinear transformation decomposes reaction invariants into flow variants and reaction and flow invariants.

Various implications of reaction variants and invariants have been studied in the literature. The fact that reaction invariants are independent of the reaction progress has been exploited in the areas of process analysis, design and control. For example, the importance of reaction invariants for state observability and state controllability of continuous stirred-tank reactors has been pointed out in [5, 6, 31]. Waller and Mäkilä [96] demonstrated the role of reaction-invariant relationships such as the atomic matrix to compute the reaction invariants and subsequently to control pH. In contrast to reaction invariants, reaction variants vary with the progress of reaction. Control laws using reaction variants have been computed from linearized continuous stirred-tank reactor models in [40]. Srinivasan et al. [75] studied the implications of reaction and flow variants/invariants for control-related tasks such as model reduction, state accessibility, state reconstruction, and feedback linearizability. Bonvin and Rippin [15] used reaction variants in batch reactors for the determination of stoichiometry models without knowledge of the reaction kinetics.

The reaction variants and invariants proposed in the literature for the case of reactors with inlet and/or outlet streams are based on the ensemble of reactions and streams and thus represent a *space property*. In other words, the reaction variants and invariants are merely mathematical quantities that are devoid of any physical meaning and describe an abstract space. However, only in batch reactors, due to the absence of inlet and outlet streams, does each reaction variant correspond to the extent of a particular reaction [96]. Hence, the concept of reaction variant in batch reactors represents an *individual property*.

The concept of extent of reaction is useful to describe the behavior of chemical reactions. 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 system [21]. This fact is used to express reaction progress and handle chemical equilibrium [19, 30, 73]. The fact that the reaction variants in batch reactors represent true extents of reaction has been used for modeling reaction systems.

1.2.2 Reduced-order models

Since detailed models of reaction systems contain a large number of states with widely varying dynamics, they are difficult to use straightforwardly in many applications. These models often contain a large number of either redundant or negligible dynamic elements. Model-order reduction can be used to eliminate both redundant and negligible elements, thus simplifying the model and providing deeper insight into the reaction system [42, 60]. In the literature, the three approaches, lumping, time-scale analysis and sensitivity analysis, are routinely applied to reduce the model order [42, 60, 94]. In lumping, the original state vector is transformed into a lower-dimensional state vector by linear or nonlinear functions [51, 52, 53, 88]. Hence, the transformed states are linear or nonlinear combinations of the original states. Time-scale analysis exploits the multiple time scales in reaction dynamics exhibited by fast and slow reactions. The fast reactions can be considered at quasi-steady-state relative to the slow reactions and thus the model order can be reduced by keeping the slow modes and eliminating the fast ones [34, 57, 60, 94]. On the other hand, sensitivity analysis examines the dynamic behavior of reaction systems with respect to disturbances, and identifies the important species and reactions [45, 62, 90]. Then, a reduced model is obtained by eliminating the insignificant species and redundant reactions. All these reduction methods require sufficient information regarding the kinetic model. Note also that physical information about species and reactions is lost in the reduced models.

1.2.3 Identification of reaction systems

The identification of reaction systems involves two steps, namely the identification of a model structure and the estimation of model parameters from experimental data. In model-based experimental analysis, measurements of concentrations, calorimetry and spectra (NIR, MIR, UV/VIS, etc.) are obtained from experiments that are planned based on some prior knowledge about the reaction system of interest. Analysis methods such as multivariate calibration (MVC) and multivariate curve resolution (MCR) are used to estimate concentrations based on spectral data [55]. An experienced human modeler can propose a model structure (e.g. possible stoichiometries and reaction-rate expressions) from prior knowledge, and estimated and measured key variables. Parameter estimation is then applied to estimate the unknown parameters in each of the proposed models based on experimental data and/or the estimated key variables. The model that ‘best’ fits the data (typically in terms of weighted least-squares error) is selected as the best model. If this model does not describe the data satisfactorily, new experiments are planned based on this model. Iterative improvements of the experiments and the model are carried out to generate an acceptable kinetic model.

Various methods and frameworks for the analysis of measured data in the literature can be divided into two classes depending on the type of measured data. The first class consists of the methods that use spectral and calorimetric data, while the second one

consists of the methods and frameworks that use concentrations and calorimetric data. In the following sections, these two classes of methods are described.

1.2.3.1 Use of spectral and calorimetric data

Analysis methods for spectral and calorimetric data can be classified into three main groups: soft-modeling methods, hard-modeling methods, and hybrid-modeling methods.

Soft-modeling methods

Soft-modeling methods, such as MVC or MCR, allow us to analyze spectral data from reaction systems without knowledge of a kinetic model. Soft-modeling methods estimate concentrations and pure-component spectra based on spectral data. Then, the concentrations estimated using soft-modeling methods can be used for investigating reaction systems.

MVC methods develop a calibration model based on spectra data and the corresponding reference concentrations [18]. Methods such as principal component regression (PCR), partial least squares (PLS), neural networks, support vector machines, or projection pursuit are often used to build the calibration model [89, 95, 99]. This calibration model can then be applied to spectra from mixtures of unknown concentrations to predict the concentration values in some prediction intervals.

When reference concentrations are not available, MCR methods (including factor-analytical methods, FA) can be used to resolve the unknown concentration profiles from spectral data and some prior knowledge. MCR involves two steps: (i) decomposition of the spectral data matrix into abstract factors using principal component analysis (PCA), and (ii) rotation of these abstract factors into physically meaningful concentration profiles and pure-component spectra by methods such as alternative least-squares (ALS) [55]. For this rotation, prior knowledge about the underlying system and the type of instrumental response is required. This prior knowledge must be carefully translated into constraints such as non-negativity of concentrations and pure-component spectra, unimodality of certain types of concentration profiles such as hyphenated data, and mass balance closure condition in order to overcome the rotational ambiguity in Step (ii) [32, 86]. Multivariate curve resolution-alternative least square (MCR-ALS) is a constrained optimization algorithm that takes into account these constraints to recover the true underlying concentration profiles and pure-component spectra from spectral data [84]. Tauler [83] proposed a new MCR method that minimizes an unconstrained nonlinear function formulated directly from the constraints non-fulfillment and being in the subspace spanned by the abstract factors obtained in Step (i). The unconstrained nonlinear function has large values when the constraints are not fulfilled, while it has values close to zero when the constraints are nearly or totally fulfilled [83]. The MCR method based on this unconstrained function is called MCR-FMIN in [83]. However, the constraints applied in MCR methods rarely guarantee a unique solution, and a set of feasible solutions are also possible [23]. Hence, in practice, finding and applying appropriate constraints that overcome the ambiguity are key elements in en-

hancing the MCR-based techniques [23, 33, 86]. Moreover, it is of great interest to check whether rotational ambiguity is present in the solutions obtained using MCR methods. A method to evaluate the possible rotational ambiguity in the solutions obtained using MCR methods has been proposed [82, 83]. This method can also check how different the true solution can be from that obtained by MCR methods.

MCR methods can estimate the concentration profiles of the absorbing species and the pure component spectra under the assumption that the rank of the spectral data matrix is equal to the number of absorbing species [71]. For reaction systems, however, the spectral data matrices are typically rank deficient due to the underlying reactions, i.e. the corresponding rank is less than the number of absorbing species [2, 3]. MCR applied to such rank-deficient spectral data leads to invalid estimates of concentration profiles. Fortunately, the problem of rank deficiency can be solved by rank augmentation such as appending data obtained from several experiments and/or adding amounts ('spike') of certain species during the experimental run [3].

Hard-modeling methods

Hard-modeling methods involve fitting a kinetic model directly to the spectral data [2, 54, 80, 85]. The contributions of inlets and initial conditions can be removed from the spectral data such that the resulting *reaction-variant form* (RV-form) of the spectral data contains only the contribution of the unknown chemical reactions [2]. Using the RV-form of spectral data and a given kinetic model with unknown parameters, a constrained least-squares optimization problem has been formulated to estimate the concentration profiles and the rate parameters [2]. In contrast to soft-modeling methods such as MVC, the identified kinetic model can often be extrapolated outside the conditions used to determine the model and its parameters [65]. A constrained nonlinear least-squares problem has been proposed to simultaneously determine the concentration profiles and fit the parameters of a kinetic model to spectral data [54]. Simultaneous analysis of multi-batch spectroscopic and calorimetric data has also been proposed to fit a kinetic model and estimate the reaction heat and dissolution heat profiles [65].

The spectral and calorimetric data contain different information as well as measurement errors. A scaling procedure has been proposed to appropriately weight the fitting errors of spectroscopic and calorimetric data [102, 103]. As an alternative, an approach based on a multi-objective cost function has been proposed to estimate the parameters of a given model structure using Pareto optimal approach and a genetic algorithm [35]. The errors and uncertainties in the experimental conditions affect the rate parameters estimated using hard-modeling methods. The propagation of errors from the measured spectral data to the estimated rate parameters has been studied in [13].

Hybrid-modeling methods

Hybrid-modeling methods have been introduced to exploit the advantages of soft-modeling and hard-modeling methods [24, 25]. A kinetic model with given model structure but unknown parameters is added as a hard constraint to solve the rota-

tional ambiguity in MCR-ALS (labeled as hybrid MCR-ALS). Hybrid MCR-ALS has also been applied to the RV-form of spectral data obtained from a batch reactor in [14].

1.2.3.2 Use of concentrations and calorimetric data

To identify the parameters of a kinetic model from concentration data, two methods can typically be distinguished: the integral and differential methods [50]. In the integral method, the given rate expression is integrated analytically or numerically to predict concentrations, and the unknown parameters are estimated by fitting these predictions to measured concentrations using constrained optimization techniques. In the differential method, the reaction rates are estimated through differentiation of concentration data, and the unknown parameters are estimated by fitting the estimated rates to the computed rates using the given rate expression.

There are advantages and disadvantages of each method. On the one hand, the integral method requires a large computational effort because integration is required at each step of the optimization procedure. On the other hand, the differential method requires differentiation of concentration measurements – a difficult task because of noise and sparsity of measurements – that calls for appropriate regularization. Note that the integral method gives optimal estimates in the maximum likelihood sense in the absence of structural uncertainty and for Gaussian measurement noise [17], while the differential method does not, due to the approximation introduced by the numerical differentiation.

The integral and differential methods used by the two modeling frameworks that are available to identify the model structure and the parameters of reaction systems: (i) global identification, and (ii) incremental identification.

Simultaneous identification

The simultaneous or global identification approach proceeds as follows. One chooses a model structure for the complete reaction system and formulates a parameter estimation problem involving a dynamic reaction model to identify the corresponding parameters. This approach is also termed ‘simultaneous identification’ since all reactions are considered simultaneously. The procedure needs to be repeated for all candidate model structures. The candidate with the best fit is usually selected. Issues like structural identifiability [97] and experimental planning [59] are important to guarantee parameter estimates with little correlation and narrow confidence intervals.

The main advantage of global identification is that it can deal with highly complex reaction and mass-transfer rates and lead to statistically optimal parameters in the maximum-likelihood sense [9]. However, the global identification approach can be computationally costly when several candidate structures are available. Furthermore, since the global model is fitted to reduce the prediction error, structural errors in some of the reactions will result in errors in other parts of the model. Finally, initialization with suitable parameter values is difficult and often gives rise to convergence problems [17] or to convergence to a local minimum.

Several variants of global identification have been proposed for the efficient identification of kinetic models from concentrations and calorimetric data [48, 72]. A framework for automatic modeling of chemical/biochemical reaction systems (TAM-C/B) based on concentrations and calorimetric data has been proposed [43, 72]. TAM uses an automatic iterative procedure that imitates the human expert in modeling reaction systems. From measured data, TAM first generates a qualitative description of the dynamic behavior of the reaction system using a fuzzy interval identification method [72]. Then, based on the resulting qualitative description, prior knowledge regarding the reaction stoichiometry and a rule-based library, TAM postulates possible rate expressions and fits the global model to the concentrations and calorimetric data.

An iterative model refinement framework has also been proposed that includes the discovery of model deficiencies from concentration data [48]. The authors suggest adding a stochastic process to selected mole balances exhibiting possible uncertainty. The mole balances with large fitted stochastic parameters are pinpointed as having model deficiencies. The modeler can then refine the pinpointed model equations.

Incremental identification

Alternatively, the identification task can be split into a sequence of subproblems such as the identification of stoichiometry and rate expressions. For each subproblem, the number of model candidates can be kept small. In addition, the information available at a given step can be used to refine the model in subsequent steps.

An incremental identification approach to identify reaction systems from concentrations has been proposed in [10, 16, 56]. Incremental identification splits the identification problem into a set of subproblems, namely the calculation of combined reaction and mass-transfer fluxes for each species, reaction stoichiometry, reaction and mass-transfer rates (without assuming any structure), and finally estimation of rate parameters, as shown in Figure 1.3 [16, 17, 56].

The combined reaction and mass-transfer flux of each species is first estimated from noisy concentrations using balance equations. Based on these fluxes, the stoichiometry can be determined using Target Factor Analysis (TFA) without knowledge of the reaction kinetics [15]. Incremental TFA has been proposed to remove the variability corresponding to an accepted reaction before continuing target testing for the other reactions [64]. This procedure allows more sensitive target testing in the case of noisy concentration measurements. Necessary and sufficient conditions have been formulated for the acceptance of stoichiometric targets [4].

Individual reaction and mass-transfer rates can be estimated without knowledge of rate expressions from the computed reaction and mass-transfer fluxes through differentiation of concentrations and using information regarding reaction stoichiometry and the species transferring between phases [16, 58]. Then, each estimated rate profile can be used to discriminate between several candidate rate expressions. The rate expression with the best fit is typically retained.

If the kinetic model identified using the initial experiments is inappropriate to meet the identification goal, new experiments might have to be carried out. Hence, an iterative model identification procedure is needed, as shown in Figure 1.3.

The incremental identification approach typically uses the *differential method* of kinetic identification, whereby reaction and mass-transfer fluxes are obtained by differentiation of measured concentrations. However, a bias is typically introduced in the estimation of fluxes and thus also of the rates [10, 17]. Since the rate parameters are estimated from biased rates, the estimated parameters are not statistically optimal. Hence, in the final parameter estimation step, global identification is used to obtain statistically optimal parameters using the best model structure identified by the incremental approach. After parameter estimation, the model is validated using well-established validation techniques [8]. If the model describes the data satisfactory and the parameters are within desired confidence intervals, the model is accepted and the iterative identification process terminates. Otherwise, new experiments have to be designed and carried out to refine the current model.

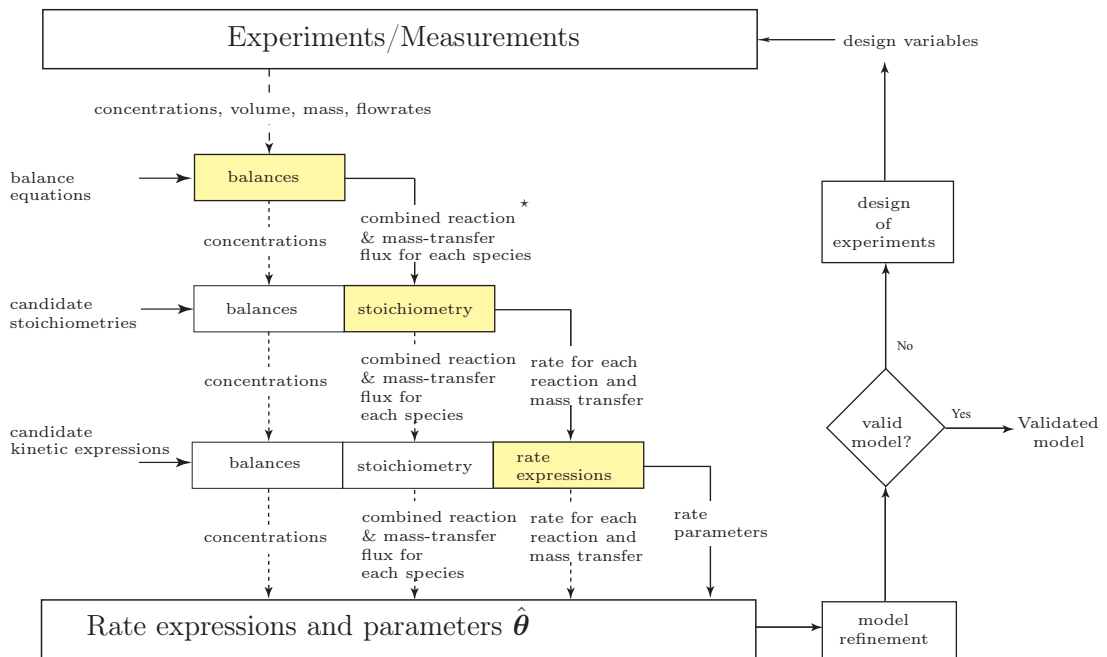


Figure 1.3 Incremental identification of rate expressions using the differential (rate-based) method (★ the computation of fluxes calls for the differentiation of concentration measurements) [16, 17].

1.3 Research objectives

This dissertation contributes to the development of the concept of extents of reaction, mass transfer and flow for homogeneous and gas-liquid chemical reaction systems with

inlets and outlets¹. These various extents are quite useful to study minimal state representation and state reconstruction in reaction systems. Procedures to compute the extents of reaction and mass transfer based on concentrations and spectral data are proposed. Furthermore, a novel incremental procedure for the identification of kinetic models from the computed extents using the *integral method* of kinetic identification is proposed.

Extents of reaction, mass transfer and flows

For homogeneous reaction systems, the mathematical three-way decomposition of the numbers of moles into reaction variants, inlet-flow variants, outlet-flow variant and invariants proposed by Srinivasan et al. [75] will be extended. The extension will eliminate the effect of the initial conditions from the reaction and flow variants, thus leading to true extents. The resulting linear transformation uses only information regarding the stoichiometry, the inlet composition and the initial conditions and, furthermore, it does not require any kinetic expressions.

Furthermore, the linear transformation will be extended to gas-liquid reaction systems. The concept of extents of reaction, mass transfer and flow will be developed successively for the liquid and gas phases using a linear transformation.

Minimal state representation and state reconstruction

The linear transformation decomposes the number of moles vector into the various extents and invariant states. Since the invariant states remain constant, they can be dropped from the transformed dynamic models, thus leading to model-order reduction. Minimal state representations of both homogeneous and gas-liquid reaction systems will be investigated using the concept of accessibility of nonlinear systems. In contrast to the reduced-order representations resulting from lumping, time-scale analysis and sensitivity analysis, the minimal state representations proposed in this work are not approximations and do not require kinetic information in the reduction step. Conditions under which the linearly transformed model is minimal state representation will be proposed.

Using these transformations, the reconstruction of unmeasured concentrations from measured concentrations and mass flowrates will be studied for both homogeneous and gas-liquid reaction systems. Furthermore, the minimal number of concentration measurements needed to reconstruct the unmeasured concentrations will also be investigated. It will be shown that the minimal number of concentration measurements needed is equal to the number of independent reactions for homogeneous reactors and the number of independent reactions and mass transfers for gas-liquid reactors.

¹ The concept of extent of reaction exists in the literature for closed reaction systems (for example, batch reactor). This dissertation extends this concept to open reaction systems, in particular to reaction systems with outlet streams.

Use of concentrations and spectral data

We will investigate the identification of reaction and mass-transfer rates using concentrations and spectral data for the case of open homogeneous and gas-liquid reaction systems. The identification task proceeds in two steps: (i) computation of the extents of reaction and mass transfer without knowledge of the reaction and mass-transfer rates, and (ii) estimation of the rate parameters for each rate individually from the computed extents.

In the first step, various procedures will be investigated to compute the extents of reaction and mass transfer using the proposed linear transformations. In the second step, the estimation problem to identify unknown rate parameters from the computed individual extents using the integral method will be formulated. Moreover, for the case of noisy concentrations, the error propagation from the concentrations to the computed extents will be studied.

For the case of spectral data with unknown pure-component spectra, data processing will be proposed to isolate the unknown reaction and mass-transfer contributions from the measured spectral data. The resulting data is called the reaction and mass-transfer variant (RMV) form of spectral data. An estimation problem will be formulated to simultaneously estimate the rate parameters from spectral data in RMV-form using the integral method. Furthermore, a way to use gas consumption data for rank augmentation will be proposed for the case where the spectral data in RMV-form is rank deficient.

1.4 Organization of the dissertation

Chapters 2 and 3 will investigate a transformation of the dynamic reaction models of homogeneous and gas-liquid reaction systems to extents of reaction, mass transfer and flow, and to invariants. Furthermore, Chapter 4 will investigate the minimal state representation and state reconstruction of homogeneous and gas-liquid reaction systems. The proposed transformations in Chapters 2–3 and the approaches developed in Chapter 4 will be applied to analyze concentrations and spectral data in Chapter 5. Special reactor configurations such as batch, semi-batch, and continuous stirred-tank reactors will be considered.

Chapter 2 considers homogeneous reaction systems with inlet and outlet streams and proposes a linear transformation of the number of moles vector to extents of reaction, extents of inlet flow, extent of outlet flow and invariants. The linear transformation for homogeneous reaction systems is extended to gas-liquid reaction systems with inlet and outlet streams in Chapter 3. In addition to extents of reaction and flow, the concept of extents of mass transfer in the gas and liquid phases is developed. Chapter 4 derives conditions under which the transformed models are minimal state representations. It also proposes approaches to reconstruct unmeasured concentrations using the minimal number of measurements. Chapter 5 develops procedures to compute the contributions of reaction and mass transfer from concentrations and spectral data. It also investigates

the identification of unknown rates from computed extents using the integral method. Chapter 6 presents concluding remarks and several future directions.

The main concepts are illustrated through simulated reaction systems. For the sake of readability, the proofs of the theorems, propositions, lemmas, and corollaries are given in the appendices.

Chapter 2

Extents of reaction and flow in homogeneous reaction systems

The mole balance equations of homogeneous reaction systems with inlet and outlet stream (also called open homogeneous reaction systems) describe the time evolution of the numbers of moles. They contain information regarding the stoichiometry and kinetics of the reaction system as well as operating conditions such as the reactor type, initial conditions, inlet concentrations, and inlet and outlet flowrates. The concept of reaction variants and invariants can be useful in the analysis of these reaction systems. However, the reaction variants and invariants are merely mathematical quantities that describe a space rather than individual true extents of reaction. The objective of this chapter is to develop a *transformation* of the numbers of moles that computes physically meaningful reaction variants and flow variants for open homogeneous reaction systems.

A novel linear transformation of the numbers of moles is proposed that leads to (i) the reaction variants, (ii) the inlet-flow variants, (iii) the outlet-flow invariant, and (iv) the invariants. This new linear transformation uses only information regarding the stoichiometry, the inlet composition and the initial conditions and, furthermore, it does not require information regarding kinetic expressions. Moreover, the proposed transformation 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*. Special reactor configurations such as batch, semi-batch and CSTR reactors are considered. Note that this linear transformation can be performed independently of the energy balance.

The resulting concept of extents of reaction can help transform measured data in such a way that the contribution of the (unknown) reactions can be separated from the other effects. Hence, kinetic investigation can be performed 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 [16]. Expressed differently, one would like to be able to analyze data measured in an open reactor as if they resulted from a batch reactor.

The mole balance equations for open homogeneous reaction systems are presented in Section 2.1 and it is shown that the mass balance equation is redundant since mass can be computed from the numbers of moles and molecular weights of the various species. The concept of extent of reaction is defined in Section 2.1.1. Section 2.2 describes the mathematical reaction space obtained using a two-way and a three-way decomposition of the numbers of moles. Then, a linear transformation of the numbers of moles is

proposed and used to derive the concepts of extents of reaction and of inlet and outlet flows in Section 2.3. 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 in Section 2.4.

2.1 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, as shown in Figure 2.1, can be written generically as follows:

$$\dot{\mathbf{n}}(t) = \mathbf{N}^T V(t) \mathbf{r}(t) + \mathbf{W}_{in} \mathbf{u}_{in}(t) - \frac{u_{out}(t)}{m(t)} \mathbf{n}(t), \quad \mathbf{n}(0) = \mathbf{n}_0, \quad (2.1)$$

where \mathbf{n} is the S -dimensional vector of numbers of moles, \mathbf{r} the R -dimensional reaction rate vector, \mathbf{u}_{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, $\mathbf{W}_{in} = \mathbf{M}_w^{-1} \check{\mathbf{W}}_{in}$ the $S \times p$ inlet-composition matrix with \mathbf{M}_w the S -dimensional diagonal matrix of molecular weights and $\check{\mathbf{W}}_{in} = [\check{\mathbf{w}}_{in}^1, \dots, \check{\mathbf{w}}_{in}^p]$ with $\check{\mathbf{w}}_{in}^k$ being the S -dimensional vector of weight fractions of the k th inlet stream, and \mathbf{n}_0 the S -dimensional vector of initial numbers of moles. The flowrates $\mathbf{u}_{in}(t)$ and $u_{out}(t)$ are considered as independent (input) variables in Eq. (2.1). The way these variables are adjusted depends on the particular experimental situation; for example, some elements of \mathbf{u}_{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:

$$\dot{m}(t) = \mathbf{1}_p^T \mathbf{u}_{in} - u_{out}, \quad m(0) = m_0, \quad (2.2)$$

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

$$m(t) = \mathbf{1}_S^T \mathbf{M}_w \mathbf{n}(t). \quad (2.3)$$

From the relationships $\mathbf{1}_S^T \mathbf{M}_w \mathbf{N}^T = \mathbf{0}_R$ and $\mathbf{1}_S^T \mathbf{M}_w \mathbf{W}_{in} = \mathbf{1}_p^T$, Eq. (2.2) can be obtained by differentiation of Eq. (2.3). Hence, the continuity equation Eq. (2.2) becomes redundant.

Model (2.1) is simply a mole balance for a homogeneous single-phase reaction system with several inlet streams and one outlet stream. The model holds for single-phase reaction systems, both gas and liquid, isothermal or not, since 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 $\mathbf{u}_{in}(t)$ and $u_{out}(t)$. Because the transformations developed in the next sections need only information regarding the stoichiometric matrix \mathbf{N} , the inlet-composition matrix \mathbf{W}_{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 B. 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 2.1.

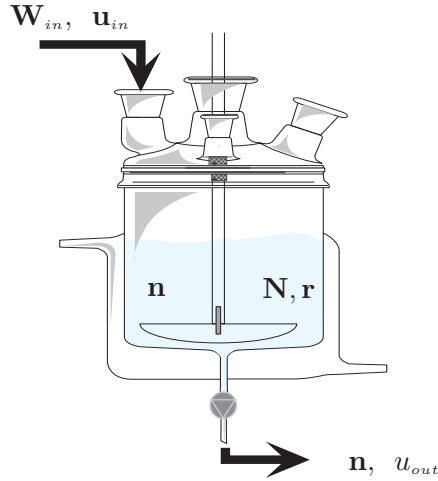


Figure 2.1 Schematic diagram of a homogeneous reaction system with p inlets and one outlet

Table 2.1 Models of batch reactor, semi-batch reactor, CSTR during transient, and CSTR at steady state (SS).

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

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

Definition 2.1 (Independent reactions)

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

Definition 2.2 (Independent inlets)

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

Amrhein [2] presents transformations of dependent reactions or inlets into independent ones.

2.1.1 Extents of reaction

For a reaction system with S species and R independent reactions, the change in *extent of reaction* for the i th reaction, $d\xi_i$, is defined as [73]:

$$d\xi_i := \frac{dn_{s,i}}{\nu_{s,i}}, \quad \forall s = 1, \dots, S, \quad \forall i = 1, \dots, R, \quad (2.4)$$

where $dn_{s,i}$ is the variation of the number of moles of the s th species caused by the i th 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. (2.4) can be directly applied to reactors without outlet stream (batch or semi-batch), for which the extent of i th reaction $\xi_i(t)$ satisfies:

$$\dot{\xi}_i(t) = V(t) r_i(t), \quad \xi_i(0) = 0. \quad (2.5)$$

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 s th species caused by the i th reaction needs to account for the outlet term. A mole balance for $n_{s,i}$ involving the reaction and outlet terms gives:

$$\dot{n}_{s,i} = \nu_{s,i} V r_i - \frac{u_{out}}{m} n_{s,i}. \quad (2.6)$$

Combining Eqs. (2.4) and (2.6) allows expressing the extent of reaction $\xi_i(t)$ that considers only the material still in the reactor:

$$\dot{\xi}_i(t) := V(t) r_i(t) - \frac{u_{out}(t)}{m(t)} \xi_i(t), \quad \xi_i(0) = 0. \quad (2.7)$$

Note that the definition in Eq. (2.7) also encompasses that in Eq. (2.5) for reactors with no outlet stream ($u_{out}(t) = 0$). 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 $\xi_i(t)$, $i = 1, \dots, R$, in Eq. (2.7) represent precisely what is needed for kinetic investigation.

Eqs. (2.5) and (2.7) 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 extents $\xi(t)$ from Eqs. (2.5) or (2.7) but from $\mathbf{n}(t)$, i.e. without reaction kinetics information.

2.2 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 decomposed into an R -dimensional reaction space and an $(S - R)$ -dimensional reaction invariant space.

Definition 2.3 (Reaction variants)

Any set of R linearly independent variables that evolve in the reaction space constitutes a reaction variant set.

Definition 2.4 (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.

2.2.1 Two-way decomposition: Reaction variants and invariants using a linear transformation

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 2.2a. Indeed, the linear transformation

$$\mathbf{n} \longrightarrow \begin{bmatrix} \mathbf{y}_r \\ \mathbf{y}_{iv} \end{bmatrix} = \begin{bmatrix} \mathbf{N}^{\text{T}+} \\ \mathbf{P}^{\text{T}} \end{bmatrix} \mathbf{n} \quad (2.8)$$

brings Eq. (2.1) to:

$$\begin{aligned} \dot{\mathbf{y}}_r &= V \mathbf{r} + \mathbf{N}^{\text{T}+} \mathbf{W}_{in} \mathbf{u}_{in} - \frac{u_{out}}{m} \mathbf{y}_r, & \mathbf{y}_r(0) &= \mathbf{N}^{\text{T}+} \mathbf{n}_0, & \text{(reaction variants)} \\ \dot{\mathbf{y}}_{iv} &= \mathbf{P}^{\text{T}} \mathbf{W}_{in} \mathbf{u}_{in} - \frac{u_{out}}{m} \mathbf{y}_{iv}, & \mathbf{y}_{iv}(0) &= \mathbf{P}^{\text{T}} \mathbf{n}_0, & \text{(reaction invariants)} \end{aligned} \quad (2.9)$$

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:

$$\mathbf{n}(t) = \mathbf{N}^T \mathbf{y}_r(t) + \mathbf{P} \mathbf{y}_{iv}(t). \quad (2.10)$$

Eq. (2.9) shows that the reaction term \mathbf{r} affects only the reaction variants \mathbf{y}_r . However, since 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.

2.2.2 Three-way decomposition: Reaction variants, inlet-flow variants, and invariants using a linear transformation

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

$$\mathbf{n} \longrightarrow \begin{bmatrix} \mathbf{z}_r \\ \mathbf{z}_{in} \\ \mathbf{z}_{iv} \end{bmatrix} = \begin{bmatrix} \mathbf{S}^T \\ \mathbf{M}^T \\ \mathbf{Q}^T \end{bmatrix} \mathbf{n}, \quad (2.11)$$

such that Eq. (2.1) becomes:

$$\begin{aligned} \dot{\mathbf{z}}_r &= \underbrace{\mathbf{S}^T \mathbf{N}^T}_{\mathbf{I}_R} V \mathbf{r} + \underbrace{\mathbf{S}^T \mathbf{W}_{in}}_{\mathbf{0}_{R \times p}} \mathbf{u}_{in} - \frac{u_{out}}{m} \mathbf{z}_r, & \mathbf{z}_r(0) &= \mathbf{S}^T \mathbf{n}_0, \\ \dot{\mathbf{z}}_{in} &= \underbrace{\mathbf{M}^T \mathbf{N}^T}_{\mathbf{0}_{R \times R}} V \mathbf{r} + \underbrace{\mathbf{M}^T \mathbf{W}_{in}}_{\mathbf{I}_p} \mathbf{u}_{in} - \frac{u_{out}}{m} \mathbf{z}_{in}, & \mathbf{z}_{in}(0) &= \mathbf{M}^T \mathbf{n}_0, \\ \dot{\mathbf{z}}_{iv} &= \underbrace{\mathbf{Q}^T \mathbf{N}^T}_{\mathbf{0}_{(S-R-p) \times R}} V \mathbf{r} + \underbrace{\mathbf{Q}^T \mathbf{W}_{in}}_{\mathbf{0}_{(S-R-p) \times p}} \mathbf{u}_{in} - \frac{u_{out}}{m} \mathbf{z}_{iv}, & \mathbf{z}_{iv}(0) &= \mathbf{Q}^T \mathbf{n}_0, \end{aligned} \quad (2.12)$$

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. (2.12), 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. [75] proposed a nonlinear transformation that satisfies the conditions given in Eq. (2.12) (See Appendix D). 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. In the next section, a novel linear transformation will be proposed.

Theorem 2.1 (Linear transformation to reaction variants and flow variants)
Consider a homogeneous reaction system involving S species, R independent reactions, p independent inlets and one outlet, and let $\text{rank}([\mathbf{N}^T, \mathbf{W}_{in}]) = R + p$. Then, the linear transformation

$$\mathbf{n} \longrightarrow \begin{bmatrix} \mathbf{z}_r \\ \mathbf{z}_{in} \\ \mathbf{z}_{iv} \end{bmatrix} = \begin{bmatrix} \mathbf{S}^T \\ \mathbf{M}^T \\ \mathbf{Q}^T \end{bmatrix} \mathbf{n} \quad (2.13)$$

brings Eq. (2.1) to:

$$\begin{aligned} \dot{\mathbf{z}}_r &= V\mathbf{r} - \frac{u_{out}}{m} \mathbf{z}_r, & \mathbf{z}_r(0) &= \mathbf{S}^T \mathbf{n}_0, & (\text{reaction variants}) \\ \dot{\mathbf{z}}_{in} &= \mathbf{u}_{in} - \frac{u_{out}}{m} \mathbf{z}_{in}, & \mathbf{z}_{in}(0) &= \mathbf{M}^T \mathbf{n}_0, & (\text{inlet-flow variants}) \\ \dot{\mathbf{z}}_{iv} &= -\frac{u_{out}}{m} \mathbf{z}_{iv}, & \mathbf{z}_{iv}(0) &= \mathbf{Q}^T \mathbf{n}_0. & (\text{reaction and inlet-flow invariants}) \end{aligned} \quad (2.14)$$

\mathbf{z}_r is the R -dimensional vector of reaction variants expressed in kmol, \mathbf{z}_{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 C. The numbers of moles \mathbf{n} in the reactor at time t can be computed from $\mathbf{z}_r(t)$, $\mathbf{z}_{in}(t)$ and $\mathbf{z}_{iv}(t)$ as follows:

$$\begin{bmatrix} \mathbf{z}_r \\ \mathbf{z}_{in} \\ \mathbf{z}_{iv} \end{bmatrix} \longrightarrow \mathbf{n}(t) = \mathbf{N}^T \mathbf{z}_r(t) + \mathbf{W}_{in} \mathbf{z}_{in}(t) + \mathbf{Q} \mathbf{z}_{iv}(t). \quad (2.15)$$

(See Proof in Appendix A.1)

Interpretation of three-way decomposition.

The three-way decomposition illustrated in Figure 2.2b can be interpreted as follows. $\mathbf{N}^T \mathbf{N}^{T+}$, $\mathbf{W}_{in} \mathbf{W}_{in}^+$ and $\mathbf{Q} \mathbf{Q}^T$ represent the reaction, inlet-flow, and reaction and inlet-flow invariant spaces, respectively. By construction, $\mathbf{Q} \mathbf{Q}^T$ is orthogonal to both the reaction and inlet spaces, which leads to $\mathbf{Q}^T \mathbf{N}^T = \mathbf{0}$ and $\mathbf{Q}^T \mathbf{W}_{in} = \mathbf{0}$ in Eq. (2.12), and thus \mathbf{z}_{iv} is independent of \mathbf{r} and \mathbf{u}_{in} . Furthermore, since the reaction and inlet spaces are not orthogonal to each other, the inlet space is rotated to give the rotated inlet space $\mathbf{W}_{in} \mathbf{M}^T$ that fulfills the conditions $\mathbf{M}^T \mathbf{N}^T = \mathbf{0}_R$ and $\mathbf{M}^T \mathbf{W}_{in} = \mathbf{I}_p$ so that \mathbf{z}_{in} is independent of \mathbf{r} and the inlet-flow variants are decoupled. Finally, since the reaction space $\mathbf{N}^T \mathbf{N}^{T+}$ is not orthogonal to $\mathbf{W}_{in} \mathbf{M}^T$, the projection $(\mathbf{I}_S - \mathbf{W}_{in} \mathbf{M}^T)$ is introduced to make the reaction space $\mathbf{N}^T \mathbf{S}^T$ orthogonal to the rotated inlet space, thus giving $\mathbf{S}^T = \mathbf{N}^{T+}(\mathbf{I}_S - \mathbf{W}_{in} \mathbf{M}^T)$ and $\mathbf{S}^T \mathbf{N}^T = \mathbf{I}_R$. It follows that \mathbf{z}_r is independent of \mathbf{u}_{in} and the reaction variants are decoupled. Note that the vectors \mathbf{z}_{in} and \mathbf{z}_{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}_{in} and \mathbf{z}_{iv} as seen in Eq. (2.14). The linear transformation in Theorem 2.1 can be visualized

by rewriting Eq. (2.15) with the help of Eq. (2.13):

$$\mathbf{n} = [\mathbf{N}^T \mathbf{S}^T + \mathbf{W}_{in} \mathbf{M}^T + \mathbf{Q} \mathbf{Q}^T] \mathbf{n} = \mathbf{I}_S \mathbf{n}. \quad (2.16)$$

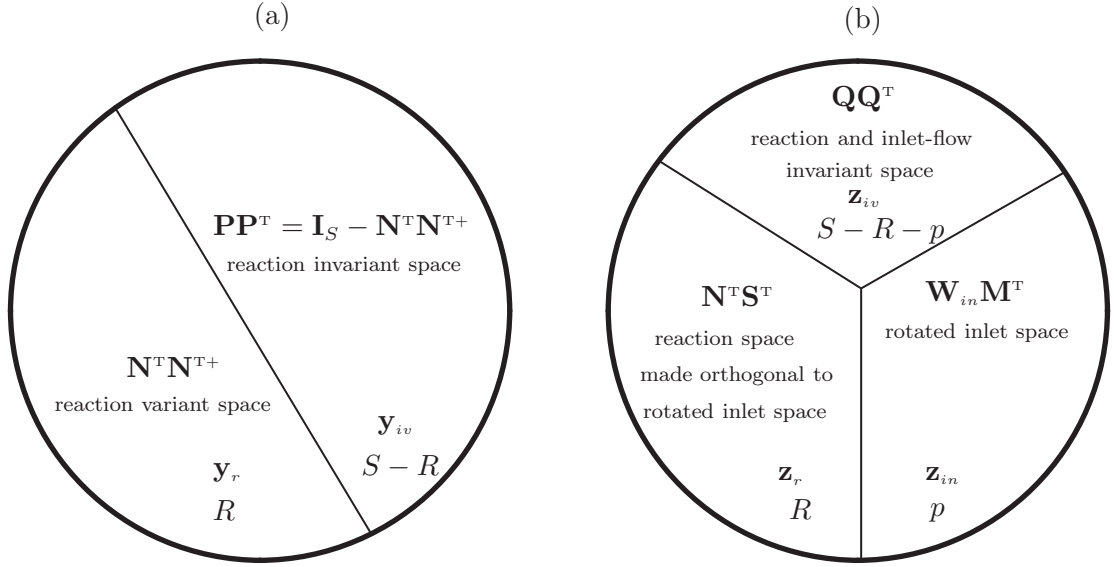


Figure 2.2 Transformation of the S -dimensional space of numbers of moles. (a) Mathematical two-way decomposition of the S -dimensional space of numbers of moles into the R -dimensional reaction variant space and the $(S - R)$ -dimensional reaction invariant space. The two spaces are orthogonal to each other with $\mathbf{N}^T \mathbf{N}^{T+} + \mathbf{P} \mathbf{P}^T = \mathbf{I}_S$. (b) Mathematical three-way decomposition of 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 $\mathbf{N}^T \mathbf{S}^T + \mathbf{W}_{in} \mathbf{M}^T + \mathbf{Q} \mathbf{Q}^T = \mathbf{I}_S$.

2.3 Linear transformation to extents of reaction and flow

The two-way and three-way decompositions presented in the previous section have generated mathematical variants and invariants that are devoid of physical meaning. For example, due to the presence of nonzero initial conditions, the reaction and inlet-flow variants in Eq. (2.14) 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 $\mathbf{n}(t)$.

2.3.1 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. (2.14). At time 0, one needs to remove the contributions $\mathbf{z}_{r,0} = \mathbf{S}^T \mathbf{n}_0$ and $\mathbf{z}_{in,0} = \mathbf{M}^T \mathbf{n}_0$. 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}_{in} and \mathbf{z}_{iv} reads:

$$\begin{bmatrix} \mathbf{z}_r \\ \mathbf{z}_{in} \\ \mathbf{z}_{iv} \end{bmatrix} \longrightarrow \begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{in} \\ \mathbf{x}_{iv} \end{bmatrix} = \begin{bmatrix} \mathbf{z}_r \\ \mathbf{z}_{in} \\ \mathbf{z}_{iv} \end{bmatrix} - \lambda \begin{bmatrix} \mathbf{z}_{r,0} \\ \mathbf{z}_{in,0} \\ \mathbf{z}_{iv,0} \end{bmatrix} \quad \text{with} \quad \lambda = \frac{\mathbf{1}_{S-R-p}^T \mathbf{z}_{iv}}{\mathbf{1}_{S-R-p}^T \mathbf{z}_{iv,0}} \quad \text{and} \quad \mathbf{1}_{S-R-p}^T \mathbf{z}_{iv,0} \neq 0, \quad (2.17)$$

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

2.3.2 From numbers of moles $\mathbf{n}(t)$ to extents $\mathbf{x}(t)$

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 . The condition $\mathbf{1}_{S-R-p}^T \mathbf{z}_{iv,0} \neq 0$ is satisfied if and only if the initial numbers of moles \mathbf{n}_0 provide information that is novel compared to the inlet-composition matrix \mathbf{W}_{in} or, in mathematical terms, \mathbf{W}_{in} and \mathbf{n}_0 are linearly independent of each other, i.e. $\text{rank}([\mathbf{W}_{in} \ \mathbf{n}_0]) = p + 1$.

Theorem 2.2 (Linear transformation to extents of reaction and flow)

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

$$\mathbf{n} \longrightarrow \begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{in} \\ \lambda \end{bmatrix} = \begin{bmatrix} \mathbf{S}_0^T \\ \mathbf{M}_0^T \\ \mathbf{q}_0^T \end{bmatrix} \mathbf{n}, \quad (2.18)$$

with

$$\mathbf{S}_0^T = \mathbf{S}^T (\mathbf{I}_S - \mathbf{n}_0 \mathbf{q}_0^T), \quad \mathbf{M}_0^T = \mathbf{M}^T (\mathbf{I}_S - \mathbf{n}_0 \mathbf{q}_0^T), \quad \mathbf{q}_0^T = \frac{\mathbf{1}_{S-R-p}^T \mathbf{Q}^T}{\mathbf{1}_{S-R-p}^T \mathbf{Q}^T \mathbf{n}_0}, \quad (2.19)$$

brings Eq. (2.1) to:

$$\begin{aligned}
 \dot{x}_{r,i} &= V r_i - \frac{u_{out}}{m} x_{r,i}, & x_{r,i}(0) &= 0, \quad \forall i = 1, \dots, R, & (\text{extents of reaction}) \\
 \dot{x}_{in,k} &= u_{in,k} - \frac{u_{out}}{m} x_{in,k}, & x_{in,k}(0) &= 0, \quad \forall k = 1, \dots, p, & (\text{extents of inlet flow}) \\
 \dot{\lambda} &= -\frac{u_{out}}{m} \lambda, & \lambda(0) &= 1. & (\text{discounting of } \mathbf{n}_0)
 \end{aligned} \tag{2.20}$$

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

$$\begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{in} \\ \lambda \end{bmatrix} \longrightarrow \mathbf{n}(t) = \mathbf{N}^T \mathbf{x}_r(t) + \mathbf{W}_{in} \mathbf{x}_{in}(t) + \mathbf{n}_0 \lambda(t). \tag{2.21}$$

(See Proof in Appendix A.2)

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 $x_{out}(t) = 1 - \lambda(t)$, with which Eq. (2.21) becomes:

$$\begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{in} \\ x_{out} \end{bmatrix} \longrightarrow \mathbf{n}(t) = \mathbf{n}_0 + \mathbf{N}^T \mathbf{x}_r(t) + \mathbf{W}_{in} \mathbf{x}_{in}(t) - \mathbf{n}_0 x_{out}(t). \tag{2.22}$$

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

2. The extent of reaction $x_{r,i}$ in Eq. (2.20) corresponds to ξ_i in Eq. (2.7), i.e. $x_{r,i} = \xi_i$
3. Transformation (2.18) uses the knowledge of \mathbf{N} , \mathbf{W}_{in} , and \mathbf{n}_0 . Note that, compared to the transformation (2.11), this transformation depends on the initial conditions \mathbf{n}_0 , hence the subscript 0 in the transformation matrices. Consequently this transformation is not one-to-one.
4. The transformed reaction system is of dimension $(R+p+1)$ and not S . The $(S-R-p)$ invariant states \mathbf{x}_{iv} are identically equal to zero and can be discarded:

$$\mathbf{x}_{iv}(t) = \mathbf{Q}_0^T \mathbf{n}(t) = \mathbf{0}_{S-R-p}, \tag{2.23}$$

- with $\mathbf{Q}_0^T = \mathbf{Q}^T(\mathbf{I}_S - \mathbf{n}_0\mathbf{q}_0^T)$ and $\text{rank}(\mathbf{Q}_0) = S - R - p - 1$. Hence, the $(S - R - p)$ invariant states \mathbf{x}_{iv} live in the $(S - R - p - 1)$ -dimensional space $\mathbf{Q}\mathbf{Q}_0^T$.
5. The matrix $(\mathbf{I}_S - \mathbf{n}_0\mathbf{q}_0^T)$ removes the contribution of \mathbf{n}_0 from \mathbf{z}_r , \mathbf{z}_{in} , and \mathbf{z}_{iv} to obtain \mathbf{x}_r , \mathbf{x}_{in} , and \mathbf{x}_{iv} . Hence, \mathbf{x}_r evolves in the R -dimensional space $\mathbf{N}^T\mathbf{S}_0^T$, \mathbf{x}_{in} in the p -dimensional space $\mathbf{W}_{in}\mathbf{M}_0^T$, and \mathbf{x}_{iv} in the $(S - R - p - 1)$ -dimensional space $\mathbf{Q}\mathbf{Q}_0^T$. λ evolves in the one-dimensional space $\mathbf{n}_0\mathbf{q}_0^T$. Note that the spaces for \mathbf{x}_r , \mathbf{x}_{in} , \mathbf{x}_{iv} and λ are *not orthogonal* to each other, but they add up to the identity matrix, i.e. $\mathbf{N}^T\mathbf{S}_0^T + \mathbf{W}_{in}\mathbf{M}_0^T + \mathbf{Q}\mathbf{Q}_0^T + \mathbf{n}_0\mathbf{q}_0^T = \mathbf{I}_S$.
 6. It is well known that a nonzero \mathbf{n}_0 never lies in the row space of \mathbf{N} [4]. Thus, the working assumption of Theorem 2.2, $\text{rank}([\mathbf{N}^T \ \mathbf{W}_{in} \ \mathbf{n}_0]) = R + p + 1$, implies $\text{rank}([\mathbf{W}_{in} \ \mathbf{n}_0]) = p + 1$.
 7. If \mathbf{n}_0 is a linear combination of the rows of \mathbf{W}_{in} , i.e. $\text{rank}([\mathbf{W}_{in} \ \mathbf{n}_0]) = p$, \mathbf{n}_0 can be modeled by an impulse inlet flowrate for the given \mathbf{W}_{in} . Hence, $\mathbf{z}_{r,0} = \mathbf{0}_R$ and $\mathbf{z}_{in,0} = \mathbf{0}_p$ in the model (2.14), which generates the extents $\mathbf{z}_r = \mathbf{x}_r$ and $\mathbf{z}_{in} = \mathbf{x}_{in}$.
 8. If $\text{rank}([\mathbf{N}^T, \mathbf{W}_{in}, \mathbf{n}_0]) < R + p + 1$, the transformation $\mathbf{n} \rightarrow \begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{in} \\ \lambda \end{bmatrix}$ defined by Eq. (2.18) does not hold, but the transformation $\begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{in} \\ \lambda \end{bmatrix} \rightarrow \mathbf{n}$ defined by Eq. (2.21) is still valid.

The linear transformation of Theorem 2.2 is illustrated in Figure 2.3. The physical interpretation of \mathbf{x}_r , \mathbf{x}_{in} , and x_{out} is discussed next.

Extents of reaction \mathbf{x}_r [kmol]

Eq. (2.20) indicates that the extent of reaction $x_{r,i}$ ($\forall i = 1, \dots, R$) is decoupled from the other extents. It can be interpreted as the number of moles that is produced by the i th reaction and remains in the reactor. The term $-\frac{u_{out}}{m}x_{r,i}$ accounts for the material produced by the i th reaction and removed from the reactor.

Extents of inlet flow \mathbf{x}_{in} [kg]

The element $x_{in,k}$ ($\forall k = 1, \dots, p$) can be interpreted as the mass added by the k th inlet that remains in the reactor. The term $-\frac{u_{out}}{m}x_{in,k}$ accounts for the material added by the k th inlet that has left the reactor.

Extent of outlet flow x_{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, $x_{out} = 0$, while with an outlet, $x_{out}(t)$ goes asymptotically to 1.

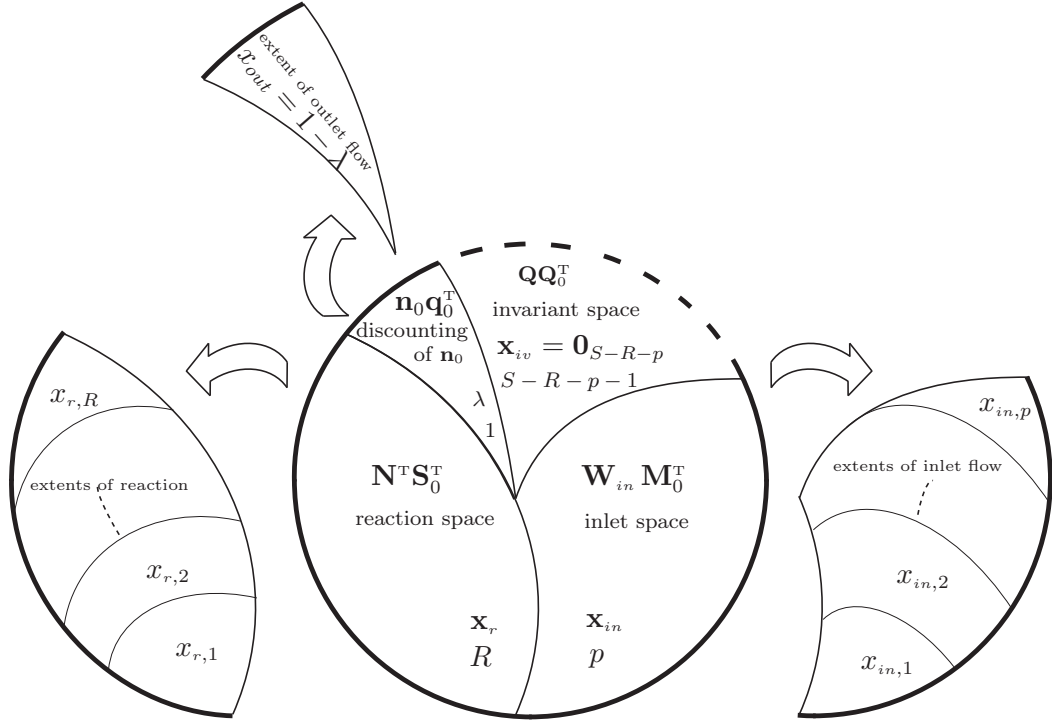


Figure 2.3 Physical three-way decomposition of the S -dimensional space of numbers of moles into an R -dimensional reaction space, a p -dimensional inlet-flow space, a one-dimensional space describing the discounting of \mathbf{n}_0 , and an $(S-R-p-1)$ -dimensional invariant space. The extents of reaction ($x_{r,i}$, $i = 1, 2, \dots, R$), extents of inlet flow ($x_{in,k}$, $k = 1, 2, \dots, p$), 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 $(\mathbf{I}_S - \mathbf{n}_0 \mathbf{q}_0^T)$; however, $\mathbf{N}^T \mathbf{S}_0^T + \mathbf{W}_{in} \mathbf{M}_0^T + \mathbf{n}_0 \mathbf{q}_0^T + \mathbf{Q} \mathbf{Q}_0^T = \mathbf{I}_S$.

2.3.3 Special reactor configurations

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

Batch reactor:

In a batch reactor, $p = 0$ and $u_{out} = 0$. It follows that $x_{out} = 0$, and Eq. (2.20) reduces to:

$$\dot{x}_{r,i} = V r_i, \quad x_{r,i}(0) = 0, \quad \forall i = 1, \dots, R. \quad (\text{extents of reaction}) \quad (2.24)$$

$x_{r,i}$ corresponds to the batch extent of the i th reaction in Eq. (2.5), i.e. the number of moles converted by the i th reaction. The dynamic system is of order R . The reconstruction of $\mathbf{n}(t)$ is given by:

$$\mathbf{n}(t) = \mathbf{n}_0 + \mathbf{N}^T \mathbf{x}_r(t). \quad (2.25)$$

Semi-batch reactor:

In a semi-batch reactor, $u_{out} = 0$. It follows that $x_{out} = 0$, and Eq. (2.20) reduces to:

$$\begin{aligned} \dot{x}_{r,i} &= V r_i, & x_{r,i}(0) &= 0, & \forall i &= 1, \dots, R, & \text{(extents of reaction)} \\ \dot{x}_{in,k} &= u_{in,k}, & x_{in,k}(0) &= 0, & \forall k &= 1, \dots, p. & \text{(extents of inlet flow)} \end{aligned} \quad (2.26)$$

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

$$\mathbf{n}(t) = \mathbf{n}_0 + \mathbf{N}^T \mathbf{x}_r(t) + \mathbf{W}_{in} \mathbf{x}_{in}(t). \quad (2.27)$$

CSTR:

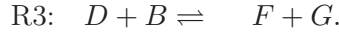
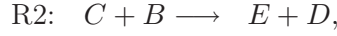
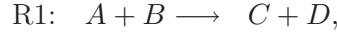
In a CSTR, $u_{out}(t)$ is computed from $V(t) = \frac{m(t)}{\rho(t)} = V_0$ and Eq. (2.2) as follows:

$$u_{out}(t) = \mathbf{1}_p^T \mathbf{u}_{in}(t) - \dot{\rho}(t) V_0, \quad (2.28)$$

where ρ is the mixture density. The extents of reaction and flow are computed from Eq. (2.20) and the reconstruction of $\mathbf{n}(t)$ is given by Eq. (2.22). 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 $u_{out}(t) = \mathbf{1}_p^T \mathbf{u}_{in}(t)$. It follows that $\lambda(t)$ can be computed algebraically from the states $\mathbf{x}_{in}(t)$ as $\lambda(t) = 1 - \frac{\mathbf{1}_p^T \mathbf{x}_{in}(t)}{m_0}$ and, thus, the state equation for λ can be removed and the dynamic system is of order $(R + p)$.

2.4 Illustrative simulated 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 ($R = 3$):



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:

$$r_1 = k_1 c_A c_B, \quad r_2 = k_2 c_B c_C, \quad r_3 = k_3 c_B c_D - k_4 c_F c_G,$$

with the reaction rate constants k_i given in Table 2.2. The molecular weights and densities of the pure species are given in Table 2.3. The vector of numbers of moles is $\mathbf{n} = [n_A, n_B, n_C, n_D, n_E, n_F, n_G]^T$. Since the reactor is considered isothermal, the density of the reaction mixture is computed as $\rho = 1 / \sum_{s=1}^S \frac{\tilde{w}_s}{\rho_s}$, with \tilde{w}_s the weight fraction of species s . Three reactor configurations will be investigated, namely a batch reactor, a semi-batch reactor, and the startup of a CSTR.

Table 2.2 Reaction rate constants (in $\text{m}^3 \text{ kmol}^{-1} \text{ h}^{-1}$).

k_1	k_2	k_3	k_4
0.127	0.023	11.97	8.01

Table 2.3 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

2.4.1 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. (2.1), (3.13) and (B.1) and are considered as noise-free measured data (see Figure 2.4a). Since 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. (2.18), i.e. without kinetic information. The extents $x_{r,1}$, $x_{r,2}$ and $x_{r,3}$ in Figure 2.4b correspond to the numbers of moles produced by reactions R1, R2, and R3, respectively. Since A is the limiting reactant and is only consumed by reaction R1, $x_{r,1}(t) = n_{A,0} - n_A(t)$ and approaches 0.2 kmol, indicating completion of reaction R1. Species C , which is produced by reaction R1 and consumed by reaction R2, limits reaction R2 shortly after reaction R1 stops. The extent $x_{r,2}$ indicates the number of moles of E that is produced by reaction R2 and also approaches 0.2 kmol, indicating completion of reaction R2. Since 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.

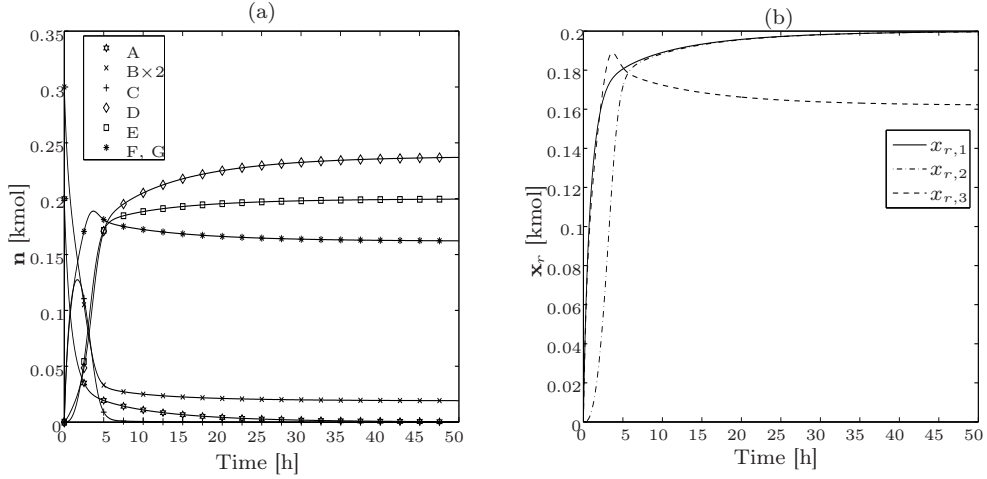


Figure 2.4 Batch reactor. Time profiles of (a) the numbers of moles \mathbf{n} , and (b) the extents of reaction \mathbf{x}_r .

2.4.2 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 $\mathbf{W}_{in} = [0 \ 0.0217 \ 0 \ 0 \ 0 \ 0 \ 0]^T \text{ kmol kg}^{-1}$ and $\text{rank}([\mathbf{N}^T \ \mathbf{W}_{in}]) = R + p = 4$ as required by Theorem 2.1. The matrices \mathbf{S} , \mathbf{M} and \mathbf{Q} are computed using the algorithm given in Appendix C.

Extents of reaction and inlet flow:

$\mathbf{n}(t)$ is simulated and considered as measured data. This is illustrated in Figure 2.5, which also shows the reactor mass computed from \mathbf{n} using Eq. (3.13). The extents of reaction \mathbf{x}_r and the extent of inlet flow x_{in} are computed using Eq. (2.18), i.e. without information regarding the kinetics and the inlet flow. As in Case 1, since 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 reaction R3 is pushed to the right side, and $x_{r,3}$ increases steadily with time, producing F and G , until full depletion of D (not shown here). As shown in Figure 2.6b, x_{in} increases steadily with time due to feeding of B .

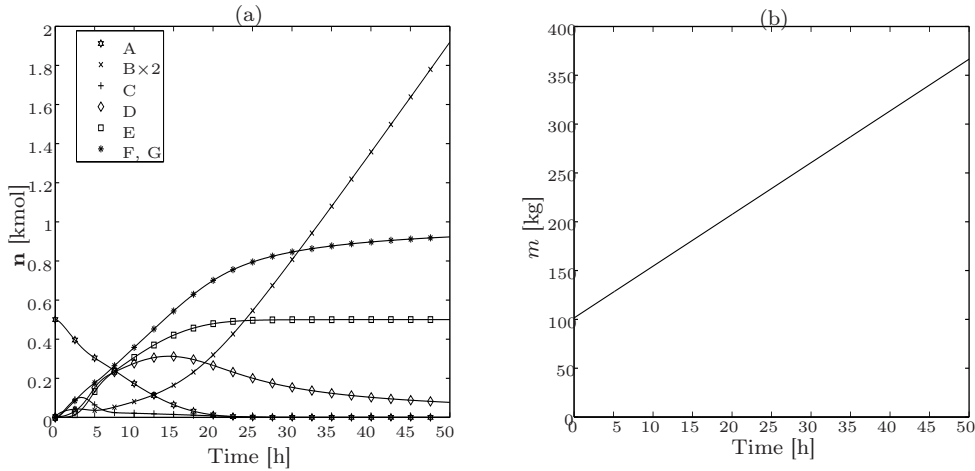


Figure 2.5 Semi-batch reactor. Time profiles of (a) the numbers of moles \mathbf{n} , and (b) the reactor mass m .

2.4.3 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 $\mathbf{W}_{in} = \begin{bmatrix} 0.0049 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.0217 & 0 & 0 & 0 & 0 \end{bmatrix}^T \text{ kmol kg}^{-1}$ and $\text{rank}([\mathbf{N}^T \mathbf{W}_{in}]) =$

$R + p = 5$. The reactor is initially filled with 1.5 kmol of ethyl chloride (F) and thus $\mathbf{n}_0 = [0, 0, 0, 0, 0, 1.5, 0]^T \text{ kmol}$. 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 $[0, 5] \text{ h}$. The time profiles of \mathbf{n} simulated using Eq. (2.1) are shown in Figure 2.7a, the mass m computed using Eq. (3.13) is shown in Figure 2.7b, and the inlet and outlet streams are shown in Figure 2.7c. 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. (2.28), decreases the outlet mass flowrate. Addition of the light species

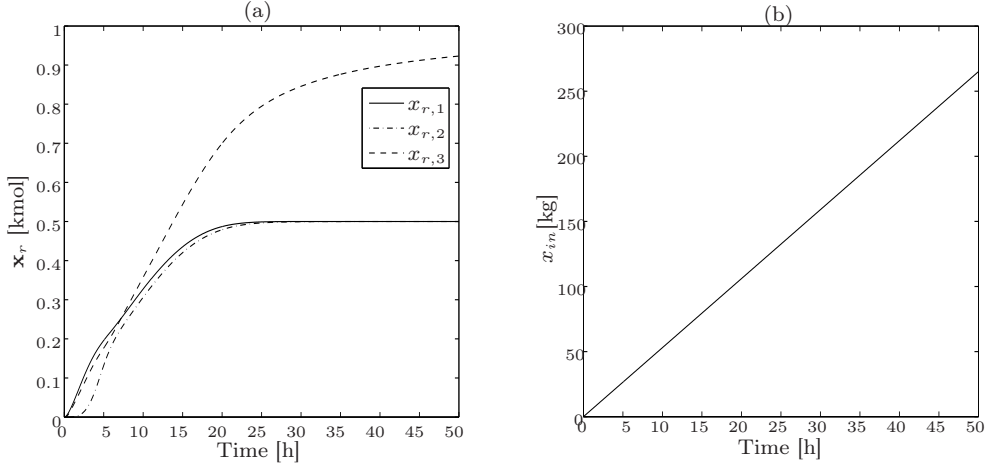


Figure 2.6 Semi-batch reactor. Time profiles of (a) the extents of reaction \mathbf{x}_r , and (b) the extent of inlet flow x_{in} .

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 (2.13) is first applied to \mathbf{n} to compute the reaction variants \mathbf{z}_r , the inlet-flow variants \mathbf{z}_{in} , and the reaction and flow invariants \mathbf{z}_{iv} (see Figure 2.8a–c). Figure 2.8a 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 $\mathbf{S}^T \mathbf{n}_0$. Similarly, $z_{in,2}$ (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 $\mathbf{M}^T \mathbf{n}_0$. Hence, unlike in batch and semi-batch reactors, the mathematical reaction variants \mathbf{z}_r and the inlet-flow variants \mathbf{z}_{in} do not represent physical extents in reaction systems with an outlet stream.

Extents of reaction and flow:

The matrices \mathbf{Q} and \mathbf{M} are computed using the algorithm given in Appendix C. Since $\text{rank}([\mathbf{N}^T \mathbf{W}_{in} \mathbf{n}_0]) = R + p + 1 = 6$ and $\mathbf{1}_{S-R-p}^T \mathbf{Q}^T \mathbf{n}_0 = 0.4160 \neq 0$, Theorem 2.2 can be applied. The extents of reaction and flow are computed from \mathbf{n} using Eq. (2.18), i.e. without information regarding the kinetics and the inlet and outlet flows. The results are shown in Figure 2.9 and discussed next:

- **Extents of reaction:** Figure 2.9a 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 2.9a). The

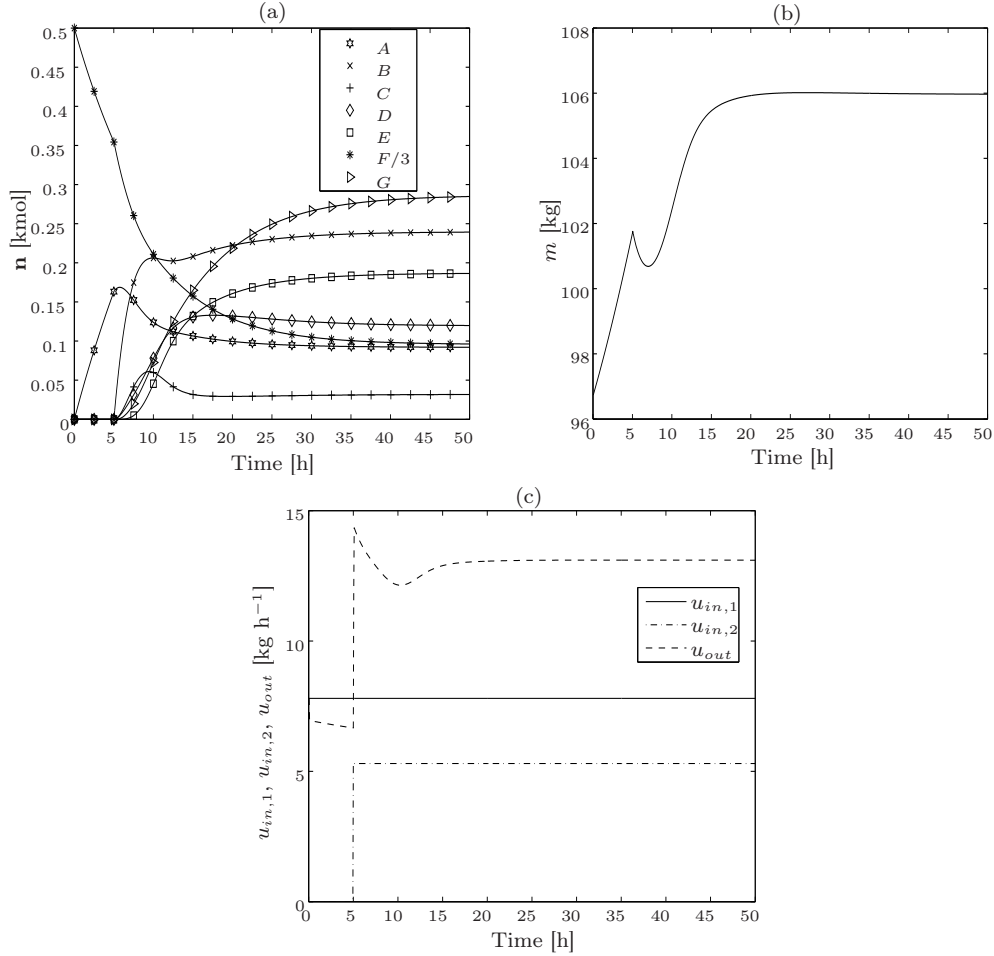


Figure 2.7 Startup of CSTR. Time profiles of (a) the numbers of moles \mathbf{n} , (b) the reactor mass m , and (c) the inlet and outlet mass flowrates $u_{in,1}$, $u_{in,2}$ and u_{out} .

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 2.9a with \mathbf{z}_r for a batch reactor in Figure 2.4b and a semi-batch reactor in Figure 2.6a.

- **Extents of inlet flow:** Fig 2.9b 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:** Fig 2.9c shows the time profiles of the outflow extent x_{out} . $x_{out}(t)$ shows the fraction of the initial numbers of moles that has left the reactor at time t . It tends asymptotically to 1, i.e. the initial amount of ethyl chloride has left the reactor after 48 h.

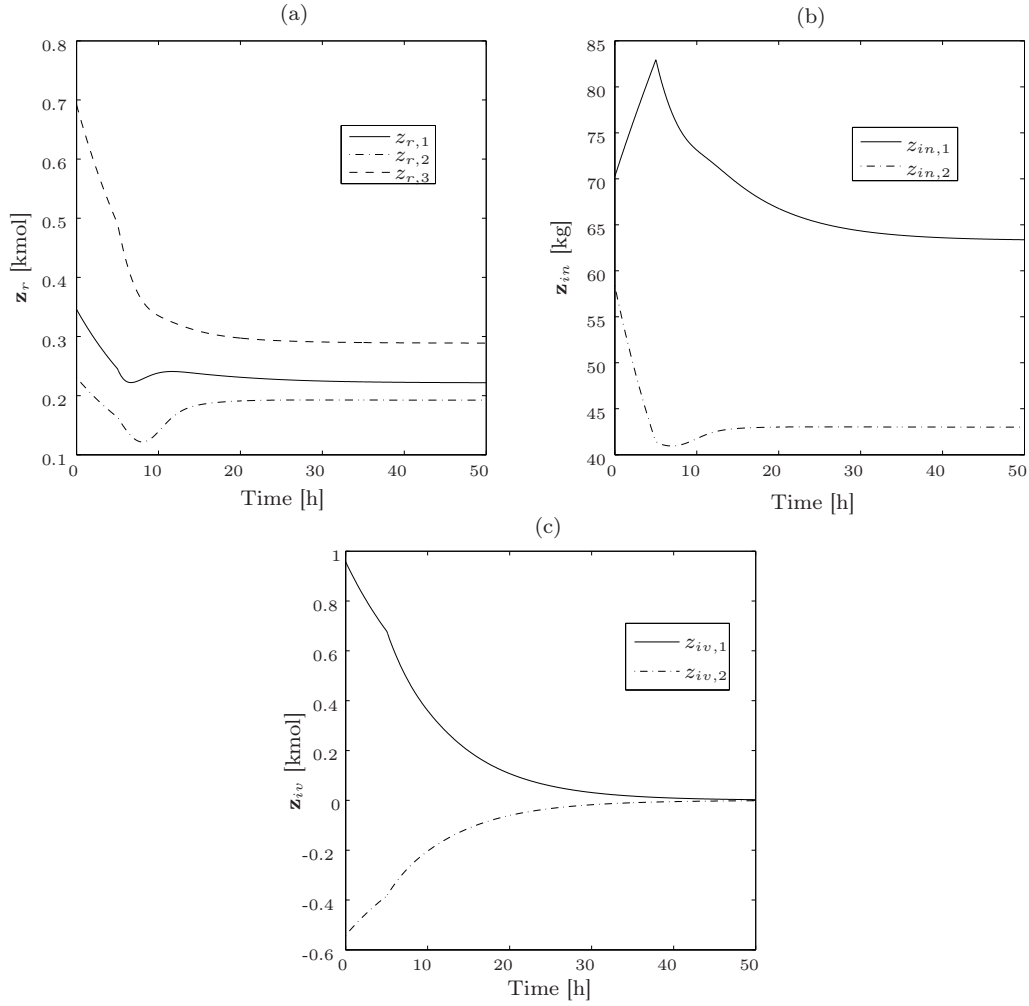


Figure 2.8 Mathematical variants in the startup of CSTR. (a) Reaction variants z_r , (b) inlet-flow variants z_{in} , and (c) reaction and inlet-flow invariants z_{iv} .

2.5 Summary

In this chapter, a linear transformation has been proposed that decomposes the numbers of moles in open homogeneous reaction systems into extents of reaction, inlet and outlet flows. 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 homogeneous reaction systems with an outlet stream; each extent of reaction represents the number of moles that is converted by the corresponding reaction and is 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

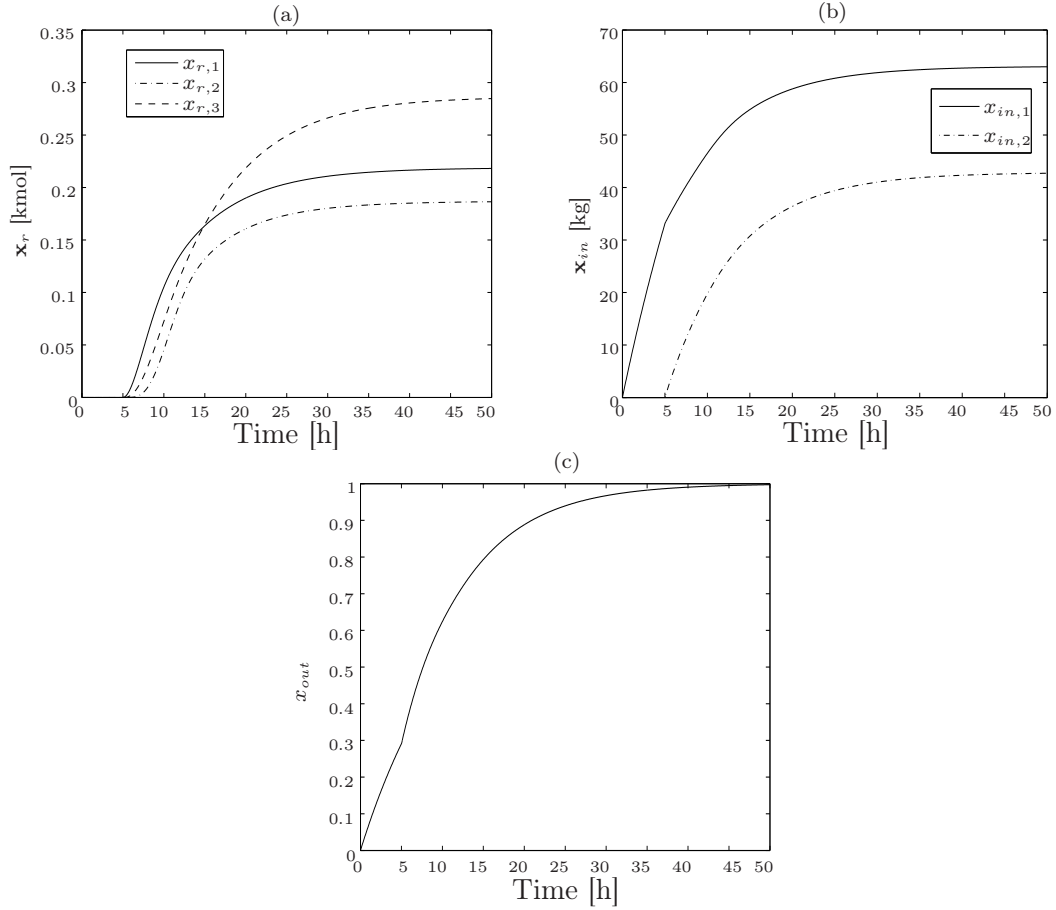


Figure 2.9 Various extents in the startup of CSTR. (a) Extents of reaction x_r , (b) extents of inlet flow x_{in} , and (c) extent of outlet flow x_{out} .

moles that has left the reactor. The ability to compute the extents of reaction and flow from the measured numbers of moles has been illustrated via the simulated study of the ethanolsysis of phthalyl chloride.

To put the present work in perspective, the transformations available in the literature and one proposed in this work are compared schematically in Fig. 3.10. 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.

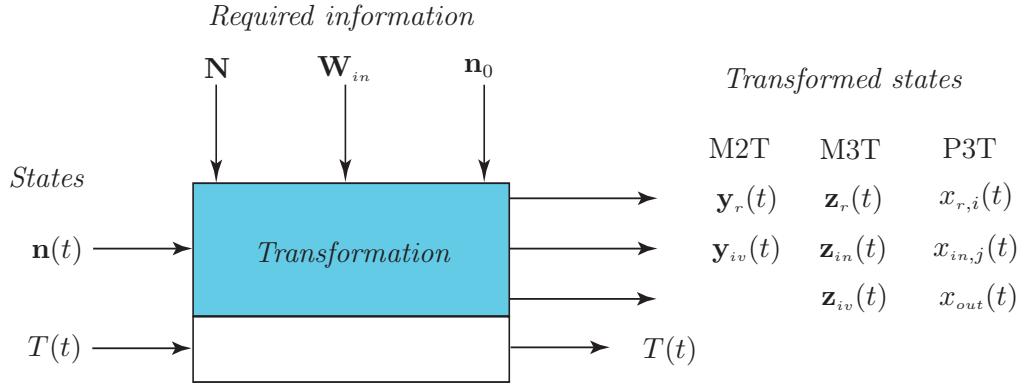


Figure 2.10 Comparison of the transformations available in the literature and that proposed in this work. All the transformations are based on the stoichiometric matrix \mathbf{N} , and if needed also on the inlet matrix \mathbf{W}_{in} and the initial conditions \mathbf{n}_0 , to transform the numbers 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 ($i = 1, \dots, R$ and $k = 1, \dots, p$). Also note that all these transformations can be performed independently of the energy balance.

Chapter 3

Extents of reaction, mass transfer and flow in gas–liquid reaction systems

Gas-liquid (G–L) reaction systems are frequent in the production of chemical and biochemical products. Often, the reactions take place in the liquid phase, as in oxidations, hydrogenations and chlorinations [38]. Compared to homogeneous reaction systems, the mass transfer between phases represents an additional element in the models of G–L reaction systems. It follows that G–L reaction systems are difficult to model because of the direct coupling between the chemical reactions and the transfer of reactants and products between the two phases. Mass transfer is often modeled as additional reactions with unknown rates in the investigation of G–L reaction systems from the measured data [58]. However, such an approach does not account for the changes in the mass of the individual phases. In this dissertation, mass transfer will be modeled as additional inlets (with unknown rates) to the gas and liquid phases.

For the analysis of G–L reaction systems, it would help to be able to separate the contributions of individual reactions and individual mass transfer from those of the inlet and outlet streams, similar to what has been done for homogeneous reaction systems in the previous chapter. Moreover, G–L reaction systems are dynamic entities that encompass several phenomena, each with its own dynamics. For example, the various reactions can have widely different time constants, or the transfer phenomena can be fast or slow relative to the reactions. Since these dynamic phenomena typically affect most of the states of the reaction system, which encompass the numbers of moles (or concentrations) and the reactor temperature, it is often not possible to discard certain states relative to others, whereas it would be fully justified to neglect certain reactions or mass transfers compared to others. Hence, it would be very useful to be able to view and describe the behavior of G–L reaction systems in terms of the contributions of each reaction, each mass transfer, and each inlet and outlet flow.

The aim of this chapter is to extend the linear transformation for homogeneous reaction systems with inlet and outlet streams proposed in Chapter 2 to *G–L reaction systems with inlet and outlet streams*. A linear transformation is proposed that decomposes the number of moles vector into five distinct parts, namely, the extents of reaction, the extents of mass transfer, the extents of inlet flow, the extents of outlet flow, and the invariants. The new concept of *extents of mass transfer* describes the contribution of individual mass transfer, independently of the contribution of the other reactions, other mass transfers and of operating conditions such as initial conditions, inlet concentrations and flowrates.

Section 3.1 revisits the two-film theory of steady-state mass transfer and develops mole balance equations for G–L reaction systems. For simplicity of presentation, it is assumed that all the reactions take place in the liquid phase. In Section 3.2, the numbers of moles in the liquid and gas phases are transformed linearly into extents of reaction, extents of mass transfer, and extents of inlet and outlet flow. Furthermore, for the cases of batch and semi-batch reactors, Section 3.2.3 shows that the linear transformation can be implemented by considering both phases simultaneously. An extension to unsteady-state mass-transfer models is presented in Section 3.2.4. The conceptual developments in this chapter are illustrated via the simulation of the chlorination of butanoic acid in Section 3.3.

3.1 Mole balance equations for gas–liquid reaction systems

Consider a G–L reaction system with S species living in the S -dimensional set of species \mathcal{S} . Among these S species, S_g species live in the gas phase, S_l species live in the liquid phase, $S_m = S_{gl} + S_{lg}$ species transfer between the two phases, with S_{gl} species transferring from the gas to the liquid and S_{lg} species transferring from the liquid to the gas. Correspondingly, the various sets of species are denoted as follows: $\mathcal{S}_g \subseteq \mathcal{S}$, $\mathcal{S}_l \subseteq \mathcal{S}$, $\mathcal{S}_m = \mathcal{S}_{gl} \cup \mathcal{S}_{lg}$, with $\mathcal{S}_{gl} \subseteq \mathcal{S}$ and $\mathcal{S}_{lg} \subseteq \mathcal{S}$.

The next three sections successively revisit the concept of steady-state mass transfer in a G–L reaction system, develop the mole balance equations for G–L reaction systems, and introduce the concept of extended inlets.

3.1.1 Steady-state mass transfer

Mass transfer is governed by interfacial phenomena that are typically difficult to observe experimentally. It will be assumed that mass transfer is at quasi steady state, i.e. there is no accumulation in the boundary layer. Models such as the stagnant two-film model, the Higbie penetration model, the surface renewal model, the film penetration model, and their modifications have been developed to describe mass-transfer phenomena [74, 87].

The two-film model illustrated in Figure 3.1 is selected here to describe the interfacial phenomena. In this model, it is assumed that the transfer resistance is limited to a boundary layer composed of two thin films around the interface. Figure 3.1a depicts the mass transfer of species $s \in \mathcal{S}_{gl}$ from the gas phase to the liquid phase, while Figure 3.1b depicts the mass transfer of species $s \in \mathcal{S}_{lg}$ from the liquid phase to the gas phase. In Figure 3.1a, the mole fraction of the s th species in the gas bulk is y_s , and it decreases to the interfacial mole fraction y_s^* at the interface. The corresponding molar concentration at the interface is c_s^* , which decreases to c_s in the liquid bulk. In Figure 3.1b, the molar concentration of the s th species in the liquid bulk is c_s , and it decreases to the interfacial concentration c_s^* . The corresponding mole fraction at the interface is y_s^* , which decreases to y_s in the gas bulk. The concentration differences in

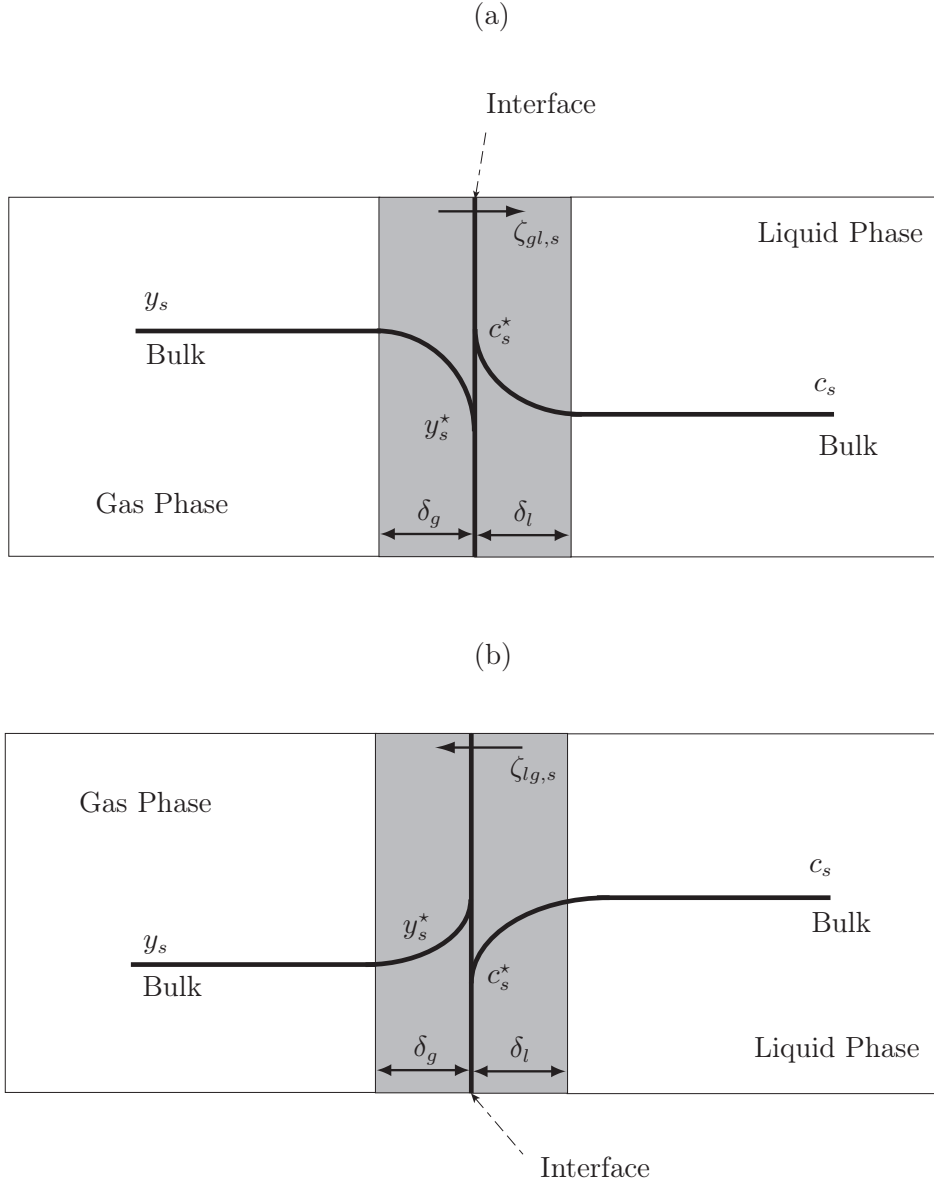


Figure 3.1 Two-film model in noninteracting mass transfer: Grey color indicates the films of thicknesses δ_g and δ_l , while white color indicates the bulk of the gas and liquid phases. As an example, (a) the s th species transfers from the gas to the liquid with the mass-transfer rate $\zeta_{gl,s}$, and (b) the s th species transfers from the liquid to the gas with the mass-transfer rate $\zeta_{lg,s}$.

the thin films are assigned to molecular diffusion of species through films of thicknesses δ_g and δ_l . The fluxes of the S_m transferring species depend on the bulk concentrations and the hydrodynamics in the films. Multicomponent mass transfer is considered next and classified into two types: (1) noninteracting multicomponent mass transfer, and (2) interacting multicomponent mass transfer.

Noninteracting multicomponent mass transfer:

In the classical approach of noninteracting multicomponent mass transfer, the mass-transfer flux of each species is assumed to be proportional to its own driving force, which is satisfied for the following practical situations [22, 74, 87]: (i) mass transfer in a binary mixture such as water/air during condensation or evaporation, (ii) mass transfer in dilute solutions such as salts, antibodies, enzymes or steroids, (iii) mass transfer of species with similar size and nature (e.g., similar diffusivities) such as close-boiling hydrocarbons or mixtures of isomers.

The molar fluxes $\xi_{gl,s}$ and $\xi_{lg,s}$ of the s th species from the gas to the liquid and from the liquid to the gas can be expressed in mole/(time)(area) units as follows:

$$\begin{aligned}\xi_{gl,s} &= f_{gl,s}(\Delta c_s) & \forall s \in \mathcal{S}_{gl}, \\ \xi_{lg,s} &= f_{lg,s}(\Delta c_s) & \forall s \in \mathcal{S}_{lg},\end{aligned}\tag{3.1}$$

where $f_{gl,s}$ and $f_{lg,s}$ are functions of the driving forces Δc_s , with $\Delta c_s = c_s^* - c_s, \forall s \in \mathcal{S}_{gl}$ and $\Delta c_s = c_s - c_s^*, \forall s \in \mathcal{S}_{lg}$.

Linear flux models are often used:

$$\begin{aligned}\xi_{gl,s} &= k_s^l(c_s^* - c_s), & s \in \mathcal{S}_{gl}, \\ \xi_{lg,s} &= k_s^l(c_s - c_s^*), & s \in \mathcal{S}_{lg},\end{aligned}\tag{3.2}$$

where k_s^l is the local low-flux (or zero-flux) molar transfer coefficients in the liquid phase [87].

Since it is difficult to measure the equilibrium concentration c_s^* at the interface, it is typically expressed as a function of the gas bulk mole fraction y_s (or partial pressure of the s th species in the reactor). Since the flux across the film is at steady state, the linear flux models in terms of the partial pressure in the gas phase can be written as follows:

$$\begin{aligned}\xi_{gl,s} &= k_s^g(\mathcal{P}_s - \mathcal{P}_s^*), & s \in \mathcal{S}_{gl}, \\ \xi_{lg,s} &= k_s^g(\mathcal{P}_s^* - \mathcal{P}_s), & s \in \mathcal{S}_{lg},\end{aligned}\tag{3.3}$$

where k_s^g is the local low-flux (or zero-flux) molar transfer coefficients in the gas phase, and \mathcal{P}_s and \mathcal{P}_s^* is the partial pressure in the bulk and the equilibrium partial pressure of the s th species, respectively. The partial pressure in the bulk can be computed from an equation of state, e.g. the ideal gas law. The equilibrium concentration can be eliminated using an equilibrium relationship such as Henry's law:

$$c_s^* = \frac{\mathcal{P}_s^*}{H_{c,s}},\tag{3.4}$$

where $H_{c,s}$ is the Henry constant for the s th species with the unit $[\text{m}^3 \text{ bar kmol}^{-1}]$. Combining Eqs. (3.2)–(3.4), the equilibrium concentration c_s^* can be expressed in terms of \mathcal{P}_s and c_s as follows:

$$c_s^* = \frac{k_s^g \mathcal{P}_s + k_s^l c_l}{k_s^g H_{c,s} + k_s^l}. \quad (3.5)$$

By substituting c_s^* in Eq. (3.5) into Eq. (3.2), the linear flux models in terms of the bulk concentration and the partial pressure in the liquid and gas phase can be written as:

$$\begin{aligned} \xi_{gl,s} &= K_{o,s}^l \left(\frac{\mathcal{P}_s}{H_{c,s}} - c_s \right) \quad s \in \mathcal{S}_{gl} \\ \xi_{lg,s} &= K_{o,s}^l \left(c_s - \frac{\mathcal{P}_s}{H_{c,s}} \right) \quad s \in \mathcal{S}_{lg}. \end{aligned} \quad (3.6)$$

where $K_{o,s}^l = \frac{1}{1/k_s^l + 1/Hk_s^g}$ is the overall molar transfer coefficient in the liquid phase.

Interacting multicomponent mass transfer:

The molar fluxes $\xi_{gl,s}$ and $\xi_{lg,s}$ in Eq. (3.1) are functions of the driving force Δc_s . However, molar fluxes often depend on the driving forces of all the species involved in mass transfer, thus giving:

$$\begin{aligned} \xi_{gl,s} &= f_{gl,s}(\Delta \mathbf{c}), \quad s \in \mathcal{S}_{gl}, \\ \xi_{lg,s} &= f_{lg,s}(\Delta \mathbf{c}), \quad s \in \mathcal{S}_{lg}, \end{aligned} \quad (3.7)$$

where $\Delta \mathbf{c}$ is the S_m -dimensional driving force vector of the S_m transferring species. Interacting multicomponent mass transfer takes place in many industrial processes such as multicomponent distillation and gas absorption. For more details, the interested reader is referred to Taylor and Krishna [87].

Remark 3.1

Note that ξ denotes a molar flux across the interface expressed in $\frac{\text{moles}}{(\text{area})(\text{time})}$ unit. Often, the modeling of G–L reaction systems makes use of mass–transfer rates in $\frac{(\text{mass})}{(\text{time})}$ unit, which can be related to molar fluxes as follows :

$$\zeta_s = \xi_s A V_l M_{w,s}, \quad s_m \in \mathcal{S}_m, \quad (3.8)$$

where A , V_l , and $M_{w,s}$ are the specific interfacial area, the liquid volume, and the molecular weight of the s th transferring species, respectively.

3.1.2 Mole balance equations for gas–liquid reaction systems with steady-state mass transfer

The mole balance equations for a G–L reaction system are presented in this section. The reactor is shown schematically in Figure 3.2. The gas and liquid phases will be modeled separately, with the mass–transfer rates ζ_{gl} and ζ_{lg} connecting the two phases.

The gas phase also contains p_g inlets and one outlet, while the liquid phase contains p_l inlets and one outlet. There are p_{gl} ($= S_{gl}$) mass–transfer fluxes from the gas to the liquid, p_{lg} ($= S_{lg}$) mass–transfer fluxes from the liquid to the gas, i.e. a total of p_m ($= S_m$) mass–transfer fluxes. Let us consider the following assumptions:

- (A1) The gas and liquid phases are homogeneous.
- (A2) The G–L reactor has a constant total volume.
- (A3) The reactions take place in the liquid bulk only.
- (A4) The mass–transfer phenomena are described by the two-film theory with no accumulation in the boundary layer. This assumption is made here for simplicity of presentation, and Section 3.2.4 discusses an extension to the case of unsteady-state mass transfer.

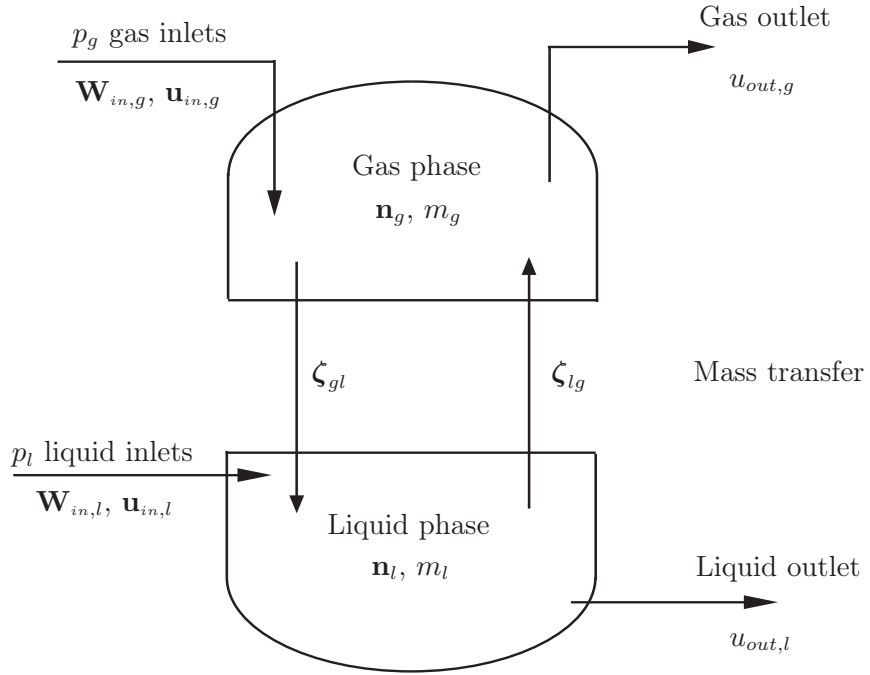


Figure 3.2 Schematic description of a G–L reaction system with two bulk phases and mass transfer between them.

The mass–transfer rates ζ_{gl} and ζ_{lg} are positive or zero. Since, by convention, the positive sign (+) is assigned to the mass transfer from the gas to the liquid, the p_m -dimensional mass–transfer rate vector is $\boldsymbol{\zeta} = \begin{bmatrix} \zeta_{gl} \\ -\zeta_{lg} \end{bmatrix}$. With these assumptions, the mole balances for the gas and liquid phases read:

Gas phase

$$\dot{\mathbf{n}}_g(t) = \mathbf{W}_{in,g} \mathbf{u}_{in,g}(t) - \mathbf{W}_{m,g} \boldsymbol{\zeta}(t) - \frac{u_{out,g}(t)}{m_g(t)} \mathbf{n}_g(t), \quad \mathbf{n}_g(0) = \mathbf{n}_{g0}, \quad (3.9)$$

Liquid phase

$$\dot{\mathbf{n}}_l(t) = \mathbf{N}^T V_l(t) \mathbf{r}(t) + \mathbf{W}_{in,l} \mathbf{u}_{in,l}(t) + \mathbf{W}_{m,l} \boldsymbol{\zeta}(t) - \frac{u_{out,l}(t)}{m_l(t)} \mathbf{n}_l(t), \quad \mathbf{n}_l(0) = \mathbf{n}_{l0}, \quad (3.10)$$

where \mathbf{n}_f is the S_f -dimensional vector of numbers of moles in the f phase, $f \in \{g, l\}$, \mathbf{N} the $R \times S_l$ stoichiometric matrix, R the number of reactions, $\mathbf{W}_{in,f} = \mathbf{M}_{w,f}^{-1} \check{\mathbf{W}}_{in,f}$ the $S_f \times p_f$ inlet matrix expressing the composition of the inlets to the f phase, $\mathbf{M}_{w,f}$ the S_f -dimensional diagonal matrix of molecular weights, and $\check{\mathbf{W}}_{in,f} = [\check{\mathbf{w}}_{in,f}^1 \cdots \check{\mathbf{w}}_{in,f}^{p_f}]$ with $\check{\mathbf{w}}_{in,f}^k$ being the S_f -dimensional vector of weight fractions of the k th inlet to the f phase with $k = 1, \dots, p_g$ for the gas inlets and $k = 1, \dots, p_l$ for the liquid inlets, $\mathbf{u}_{in,f}$ the p_f -dimensional inlet mass flowrate to the f phase, and \mathbf{n}_{f0} the vector of initial moles in the f phase. $\mathbf{W}_{m,f} = \mathbf{M}_{w,f}^{-1} \check{\mathbf{E}}_{m,f}$ is the $S_f \times p_m$ mass-transfer matrix for the f phase, $\check{\mathbf{E}}_{m,f} = [\check{\mathbf{e}}_{m,f}^1 \cdots \check{\mathbf{e}}_{m,f}^{p_m}]$ with $\check{\mathbf{e}}_{m,f}^j$ being the S_f -dimensional vector with the element corresponding to the j th transferring species equal to unity and the other elements equal to zero. Let V_t , V_l , and V_g be the total reactor volume, the liquid volume, and the gas volume, respectively. Under Assumption A2, V_t is constant and can be expressed in terms of $V_l(t)$ and $V_g(t)$ as: $V_t = V_l(t) + V_g(t)$. Thus, $V_g(t)$ can be expressed as a function of V_t and $V_l(t)$.

The relationships between mole fractions, concentrations, and numbers of moles are:

$$y_s(t) = \frac{n_{g,s}(t)}{\mathbf{1}_{S_g}^T \mathbf{n}_g(t)}, \quad \forall s = 1, \dots, S_g, \quad (3.11)$$

$$c_s(t) = \frac{n_{l,s}(t)}{V_l(t)}, \quad \forall s = 1, \dots, S_l, \quad (3.12)$$

where $\mathbf{1}_{S_g}$ is an S_g -dimensional vector filled with ones. Note that the reactor masses $m_g(t)$ and $m_l(t)$ can be inferred from the numbers of moles as:

$$m_f(t) = \mathbf{1}_{S_f}^T \mathbf{M}_{w,f} \mathbf{n}_f(t), \quad f \in \{g, l\}. \quad (3.13)$$

The flowrates $\mathbf{u}_{in,f}(t)$ and $u_{out,f}(t)$ are considered as independent (input) variables in Eqs. (3.9) and (3.10). The way these variables are adjusted depends on the particular experimental situation. For example, some of the liquid inlets can be adjusted to control the temperature in a semi-batch reactor, or the gas outlet can be adjusted to control the reactor pressure. Moreover, the liquid phase obeys Eq. (3.16) with $u_{out,l}$ specified according to the specific reactor arrangement. For example, if the liquid phase has a constant volume, the outlet mass flowrate varies with the mixture density as:

$$u_{out,l} = \mathbf{1}_{\bar{p}_l}^T \bar{\mathbf{u}}_{in,l} - \dot{\rho}_l V_l, \quad (3.14)$$

which reduces to $u_{out,l} = \mathbf{1}_{\bar{p}_l}^T \bar{\mathbf{u}}_{in,l}$ for the constant-density case, or when the reactor is operated at steady state.

Model (3.9)-(3.10) holds for both isothermal and nonisothermal reactors since the specificities regarding the reactor type and its operation are hidden in the liquid volume $V_l(t)$, the reaction rate vector $\mathbf{r}(t)$, the mass–transfer vector $\boldsymbol{\zeta}(t)$, and the specified inlet and outlet streams $\mathbf{u}_{in,f}(t)$ and $u_{out,f}(t)$. Since the transformations developed in the next two sections will require information regarding only the stoichiometric matrix \mathbf{N} , the inlet matrices $\mathbf{W}_{in,f}$, the mass–transfer matrices $\mathbf{W}_{m,f}$, and the initial conditions, these specificities do not play any role in the transformations. The specificities for both gas-phase and liquid-phase reaction systems are given in Appendix B.

3.1.3 Extended inlets

Upon grouping the inlet flowrates $\mathbf{u}_{in,f}$ and the mass–transfer rates $\boldsymbol{\zeta}$, Eqs. (3.9) and (3.10) become:

$$\dot{\mathbf{n}}_g(t) = \bar{\mathbf{W}}_{in,g} \bar{\mathbf{u}}_{in,g}(t) - \frac{u_{out,g}(t)}{m_g(t)} \mathbf{n}_g(t), \quad \mathbf{n}_g(0) = \mathbf{n}_{g0}, \quad (3.15)$$

$$\dot{\mathbf{n}}_l(t) = \mathbf{N}^T V_l(t) \mathbf{r}(t) + \bar{\mathbf{W}}_{in,l} \bar{\mathbf{u}}_{in,l}(t) - \frac{u_{out,l}(t)}{m_l(t)} \mathbf{n}_l(t), \quad \mathbf{n}_l(0) = \mathbf{n}_{l0}, \quad (3.16)$$

where $\bar{\mathbf{W}}_{in,g} = [\mathbf{W}_{in,g}, -\mathbf{W}_{m,g}]$ is a matrix of dimension $S_g \times \bar{p}_g$, $\bar{\mathbf{W}}_{in,l} = [\mathbf{W}_{in,l}, \mathbf{W}_{m,l}]$ a matrix of dimension $S_l \times \bar{p}_l$, and $\bar{\mathbf{u}}_{in,f} = \begin{bmatrix} \mathbf{u}_{in,f} \\ \boldsymbol{\zeta} \end{bmatrix}$ a vector of dimension \bar{p}_f , with $\bar{p}_f = p_f + p_m$, $f \in \{g, l\}$.

Throughout this chapter, the R reactions are assumed to be independent as per Definition 2.1. The \bar{p}_f extended inlets are assumed to be independent, according to the following definition:

Definition 3.1 (Independent extended inlets)

For the f phase, $f \in \{g, l\}$, \bar{p}_f extended inlets are said to be independent if (i) the columns of $\bar{\mathbf{W}}_{in,f}$ are linearly independent, i.e. $\text{rank}(\bar{\mathbf{W}}_{in,f}) = \bar{p}_f$, and (ii) there exists some finite time interval for which the inlet mass flowrate profiles $\bar{\mathbf{u}}_{in,f}(t)$ are linearly independent, i.e. $\boldsymbol{\beta}^T \bar{\mathbf{u}}_{in,f}(t) = 0 \Leftrightarrow \boldsymbol{\beta} = \mathbf{0}_{\bar{p}_f}$.

3.2 Linear transformation to extents of reaction, mass transfer and flow

The transformation proposed in Chapter 2 for open homogeneous reaction systems will be extended to include the extents of mass transfer. Two transformations will be developed to express \mathbf{n}_l and \mathbf{n}_g in terms of various extents as follows:

1. Linear transformation of $\mathbf{n}_l(t)$ to the extents of reaction, and the extents of mass transfer, inlet and outlet flow for the liquid phase.

2. Linear transformation of $\mathbf{n}_g(t)$ to the extents of mass transfer, inlet and outlet for the gas phase.

In addition, the special case of G–L reactors without outlet will also be considered separately.

3.2.1 Liquid phase with inlet and outlet streams

The next theorem introduces a transformation of the numbers of moles in the liquid phase to generate the corresponding extents.

Theorem 3.1 (Linear transformation to various extents)

Consider the liquid phase of the G–L reaction system given by Eq. (3.16) involving S_l species, R independent reactions, p_l independent inlets, one outlet, and p_m mass transfers between the gas and liquid phases. Let $\text{rank}([\mathbf{N}^T \ \bar{\mathbf{W}}_{in,l} \ \mathbf{n}_{l0}]) = R + \bar{p}_l + 1$. Then, the linear transformation

$$\mathbf{n}_l \longrightarrow \begin{bmatrix} \mathbf{x}_r \\ \bar{\mathbf{x}}_{in,l} \\ \lambda_l \end{bmatrix} = \begin{bmatrix} \mathbf{S}_{l0}^T \\ \bar{\mathbf{M}}_{l0}^T \\ \mathbf{q}_{l0}^T \end{bmatrix} \mathbf{n}_l \quad (3.17)$$

with

$$\mathbf{S}_{l0}^T = \mathbf{S}_l^T (\mathbf{I}_{S_l} - \mathbf{n}_{l0} \mathbf{q}_{l0}^T) = \mathbf{N}^{T+} (\mathbf{I}_{S_l} - \bar{\mathbf{W}}_{in,l} \bar{\mathbf{M}}_l) (\mathbf{I}_{S_l} - \mathbf{n}_{l0} \mathbf{q}_{l0}^T), \quad (3.18)$$

$$\bar{\mathbf{M}}_{l0}^T = \bar{\mathbf{M}}_l^T (\mathbf{I}_{S_l} - \mathbf{n}_{l0} \mathbf{q}_{l0}^T), \quad (3.19)$$

$$\mathbf{q}_{l0}^T = \frac{\mathbf{1}_{S_l-R-\bar{p}_l}^T \mathbf{Q}_l^T}{\mathbf{1}_{S_l-R-\bar{p}_l}^T \mathbf{Q}_l^T \mathbf{n}_{l0}}, \quad (3.20)$$

brings Eq. (3.16) to the extents of reaction \mathbf{x}_r , the extents of extended inlet $\bar{\mathbf{x}}_{in,l}$, and the discounting variable λ_l . The extents of extended inlet $\bar{\mathbf{x}}_{in,l}$ can be expressed in terms of the extents of mass transfer $\mathbf{x}_{m,l}$ and the extents of liquid inlet $\mathbf{x}_{in,l}$, thus leading to the following transformed mole balance equations:

$$\begin{aligned} \dot{x}_{r,i} &= V_l r_i - \frac{u_{out,l}}{m_l} x_{r,i}, & x_{r,i}(0) &= 0, \quad \forall i = 1, \dots, R, & (\text{extents of reaction}) \\ \dot{x}_{m,l,j} &= \zeta_j - \frac{u_{out,l}}{m_l} x_{m,l,j}, & x_{m,l,j}(0) &= 0, \quad \forall j = 1, \dots, p_m, & (\text{extents of mass transfer}) \\ \dot{x}_{in,l,k} &= u_{in,l,k} - \frac{u_{out,l}}{m_l} x_{in,l,k}, & x_{in,l,k}(0) &= 0, \quad \forall k = 1, \dots, p_l, & (\text{extents of liquid inlet}) \\ \dot{\lambda}_l &= -\frac{u_{out,l}}{m_l} \lambda_l, & \lambda_l(0) &= 1, & (\text{discounting of } \mathbf{n}_{l0}) \end{aligned} \quad (3.21)$$

where $x_{r,i}$ is the i th reaction extent expressed in kmol, $x_{m,l,j}$ the j th mass–transfer extent for the liquid phase expressed in kg, $x_{in,l,k}$ the extent of the k th liquid inlet expressed in kg, and λ_l the scalar dimensionless variable used to discount the effect of the initial

conditions in the liquid phase. The matrices \mathbf{S}_l , $\bar{\mathbf{M}}_l$ and \mathbf{Q}_l are computed using the algorithm given in Appendix C. The numbers of moles $\mathbf{n}_l(t)$ can be expressed in terms of the extents $\mathbf{x}_r(t)$, $\mathbf{x}_{m,l}(t)$, $\mathbf{x}_{in,l}(t)$ and the discounting variable $\lambda_l(t)$ as follows:

$$\mathbf{n}_l(t) = \mathbf{N}^T \mathbf{x}_r(t) + \mathbf{W}_{m,l} \mathbf{x}_{m,l}(t) + \mathbf{W}_{in,l} \mathbf{x}_{in,l}(t) + \mathbf{n}_{l0} \lambda_l(t). \quad (3.22)$$

(Proof follows from Theorem 2.2)

Remarks.

1. It is convenient to express the transformed system completely in terms of extents by introducing the dimensionless scalar extent of liquid outlet $x_{out,l}(t) = 1 - \lambda_l(t)$, with which Eq. (3.22) becomes:

$$\mathbf{n}_l(t) = \mathbf{n}_{l0} + \mathbf{N}^T \mathbf{x}_r(t) + \mathbf{W}_{m,l} \mathbf{x}_{m,l}(t) + \mathbf{W}_{in,l} \mathbf{x}_{in,l}(t) - \mathbf{n}_{l0} x_{out,l}(t). \quad (3.23)$$

2. Transformation (3.17) requires the knowledge of \mathbf{N} , $\bar{\mathbf{W}}_{in,l}$, and \mathbf{n}_{l0} . The subscript 0 in the matrices \mathbf{S}_{l0} , $\bar{\mathbf{M}}_{l0}$, and the vector \mathbf{q}_{l0} indicate that the transformation depends on the initial conditions \mathbf{n}_{l0} .
3. The transformed reaction system for the liquid phase is of the dimension $(R + \bar{p}_l + 1)$. In addition, there are $(S_l - R - \bar{p}_l)$ invariant states $\mathbf{x}_{iv,l}(t)$ that are identically equal to zero and can be discarded:

$$\mathbf{x}_{iv,l}(t) = \mathbf{Q}_{l0}^T \mathbf{n}_l(t) = \mathbf{0}_{S_l - R - \bar{p}_l}, \quad (3.24)$$

Note $\text{rank}(\mathbf{Q}_{l0}) = S_l - R - \bar{p}_l - 1$.

4. Note that, since a nonzero \mathbf{n}_{l0} can never lie in the row space of \mathbf{N} [4], the working assumption of Theorem 3.1, $\text{rank}([\mathbf{N}^T \bar{\mathbf{W}}_{in,l} \mathbf{n}_{l0}]) = R + \bar{p}_l + 1$, implies $\text{rank}([\bar{\mathbf{W}}_{in,l} \mathbf{n}_{l0}]) = \bar{p}_l + 1$. Also, this working assumption leads to the well-posed problem of solving for $\mathbf{x}_r(t)$, $\mathbf{x}_m(t)$, $\mathbf{x}_{in}(t)$ and $\lambda(t)$ given $\mathbf{n}_l(t)$ [93].

Interpretation of the linear transformation.

The decomposition of the S_l -dimensional space into subspaces is illustrated in Figure 3.3. The transformation can be interpreted in two steps.

In the first step, the spaces $\mathbf{N}^T \mathbf{S}_l^T$, $\mathbf{W}_{m,l} \mathbf{M}_{m,l}^T$, $\mathbf{W}_{in,l} \mathbf{M}_{in,l}^T$ and $\mathbf{Q}_l \mathbf{Q}_l^T$ shown in Figure 3.3a are obtained as follows. $\mathbf{Q}_l \mathbf{Q}_l^T$ is orthogonal to the reaction, mass-transfer and inlet spaces, which leads to $\mathbf{Q}_l^T \mathbf{N}^T = \mathbf{0}$, $\mathbf{Q}_l^T \mathbf{W}_{m,l} = \mathbf{0}$ and $\mathbf{Q}_l^T \mathbf{W}_{in,l} = \mathbf{0}$, respectively. Furthermore, since the reaction and extended-inlet spaces are not orthogonal to each other, the extended-inlet space is rotated to give the rotated extended-inlet space $\bar{\mathbf{W}}_{in,l} \bar{\mathbf{M}}_l^T$ that fulfills the conditions $\bar{\mathbf{M}}_l^T \mathbf{N}^T = \mathbf{0}_R$ and $\bar{\mathbf{M}}_l^T \bar{\mathbf{W}}_{in,l} = \mathbf{I}_{\bar{p}_l}$. The reaction space $\mathbf{N}^T \mathbf{S}_l^T$ orthogonal to $\bar{\mathbf{W}}_{in,l} \bar{\mathbf{M}}_l^T$ is obtained by introducing the rotation matrix $\mathbf{S}_l^T = \mathbf{I}_{S_l} - \bar{\mathbf{W}}_{in,l} \bar{\mathbf{M}}_l^T$. Finally, by considering the inlets and the mass transfers separately,

the rotated extended-inlet space gives the rotated mass-transfer space $\mathbf{W}_{m,l}\mathbf{M}_{m,l}^T$ and the rotated inlet space $\mathbf{W}_{in,l}\mathbf{M}_{in,l}^T$.

In the second step, the contribution of \mathbf{n}_{l0} is removed by introducing the rotation matrix $(\mathbf{I}_{S_l} - \mathbf{n}_{l0}\mathbf{q}_{l0}^T)$ to obtain the extents \mathbf{x}_r , $\mathbf{x}_{m,l}$, $\mathbf{x}_{in,l}$ and the invariant states $\mathbf{x}_{iv,l}$. These states evolve in the spaces given by $\mathbf{N}^T\mathbf{S}_{l0}^T$, $\mathbf{W}_{m,l}\mathbf{M}_{m,l0}^T$, $\mathbf{W}_{in,l}\mathbf{M}_{in,l0}^T$ and $\mathbf{Q}_l\mathbf{Q}_{l0}^T$, respectively. λ_l describes the contribution of \mathbf{n}_{l0} and evolves in the one-dimensional space given by $\mathbf{n}_{l0}\mathbf{q}_{l0}^T$. The interpretation of the various extents follows directly from Eq. (3.21) and is given next.

Extents of reaction \mathbf{x}_r [kmol]

The extent of reaction $x_{r,i}$ ($\forall i = 1, \dots, R$) is decoupled from the other extents. It can be interpreted as the number of moles that have been produced by the i th reaction and are still in the reactor. The term $-\frac{u_{out,l}}{m_l}x_{r,i}$ accounts for the material produced by the i th reaction that has been removed through the liquid outlet. Note that a negative $x_{r,i}$ value indicates the number of moles that have been consumed by the i th reaction.

Extents of mass transfer $\mathbf{x}_{m,l}$ [kg]

For a species transferring from the gas to the liquid, the extent of mass transfer $x_{m,l,j}$ ($\forall j = 1, \dots, p_{gl}$) is positive and corresponds to the mass transferred to the liquid phase that is still in the reactor. For a species transferring from the liquid to the gas, the extent of mass transfer $x_{m,l,j}$ ($\forall j = p_{gl} + 1, \dots, p_m$) is negative, with its absolute value corresponding to mass of that species that would have accumulated and remained in the liquid phase had there not been any mass transfer. The term $-\frac{u_{out,l}}{m_l}x_{m,l,j}$ accounts for the effect of the liquid outlet. A negative $x_{m,l,j}$ value indicates mass transfer in the opposite direction.

Extents of liquid inlet $\mathbf{x}_{in,l}$ [kg]

The extent of liquid inlet $x_{in,l,k}$ ($\forall k = 1, \dots, p_l$) is the mass added by the k th liquid inlet that is still in the liquid phase. The term $-\frac{u_{out,l}}{m_l}x_{in,l,k}$ accounts for the material added by the k th liquid inlet that has been removed through the liquid outlet.

Extent of liquid outlet $x_{out,l}$ [-]

The extent of liquid outlet $x_{out,l}(t) = 1 - \lambda_l(t)$ is the fraction of \mathbf{n}_{l0} that has been removed through the liquid outlet. Without liquid outlet, $\lambda_l(t) = 1$ and $x_{out,l}(t) = 0$.

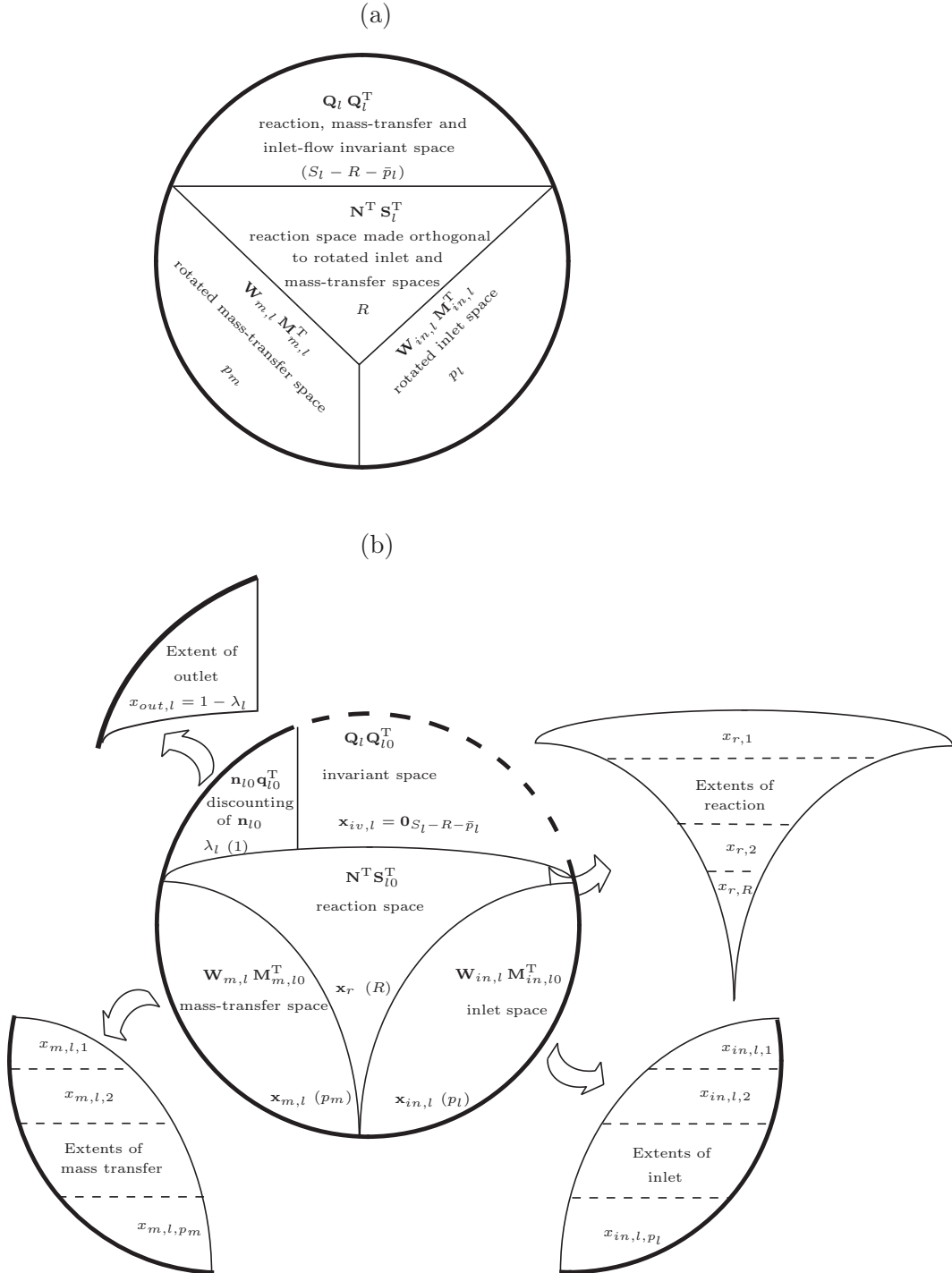


Figure 3.3 (a) Mathematical four-way decomposition of the S_l -dimensional space into *orthogonal* subspaces: a R -dimensional reaction space, a p_m -dimensional mass-transfer space, a p_l -dimensional inlet space, and a $(S_l - R - p_m - p_l)$ -dimensional invariant space. (b) Physical five-way transformation of the S_l -dimensional space into four extents spaces and one invariant space that can be discarded since the invariants are identically equal to $\mathbf{0}_{S_l - R - p_m - p_l}$. In contrast to (a), the subspaces in (b) are not necessarily orthogonal to each other due to the discounting of \mathbf{n}_{l0} through the matrix $(\mathbf{I}_{S_l} - \mathbf{n}_{l0} \mathbf{q}_{l0}^T)$. The dimension of the transformed state vector is $R + p_m + p_l + 1$.

3.2.2 Gas phase with inlet and outlet streams

The following corollary introduces a transformation of the numbers of moles in the gas phase to generate the extents of mass transfer and of gas inlet and outlet.

Corollary 3.1 (Linear transformation to various extents)

Consider the gas phase of the G - L reaction system given by Eq. (3.15) involving S_g species, p_g independent inlets, one outlet, and p_m mass transfers between the gas and liquid phases. Let $\text{rank}([\bar{\mathbf{W}}_{in,g} \ \mathbf{n}_{g0}]) = \bar{p}_g + 1$. Then, the linear transformation

$$\mathbf{n}_g \longrightarrow \begin{bmatrix} \bar{\mathbf{x}}_{in,g} \\ \lambda_g \end{bmatrix} = \begin{bmatrix} \bar{\mathbf{M}}_{g0}^T \\ \mathbf{q}_{g0}^T \end{bmatrix} \mathbf{n}_g \quad (3.25)$$

with

$$\bar{\mathbf{M}}_{g0}^T = \bar{\mathbf{M}}_g^T (\mathbf{I}_{S_g} - \mathbf{n}_{g0} \mathbf{q}_{g0}^T), \quad \mathbf{q}_{g0}^T = \frac{\mathbf{1}_{S_g - \bar{p}_g}^T \mathbf{Q}_g^T}{\mathbf{1}_{S_g - \bar{p}_g}^T \mathbf{Q}_g^T \mathbf{n}_{g0}}, \quad (3.26)$$

brings Eq. (3.15) to the extents of extended inlet $\bar{\mathbf{x}}_{in,g}$ and the discounting variable λ_g . The extents of extended inlet $\bar{\mathbf{x}}_{in,g}$ can be expressed in terms of the extents of mass transfer $\mathbf{x}_{m,g}$ and the extents of gas inlet $\mathbf{x}_{in,g}$, thus leading to the following transformed mole balance equations:

$$\begin{aligned} \dot{x}_{m,g,j} &= \zeta_j - \frac{u_{out,g}}{m_g} x_{m,g,j}, & x_{m,g,j}(0) &= 0, \forall j = 1, \dots, p_m, \text{ (extents of mass transfer)} \\ \dot{x}_{in,g,k} &= u_{in,g,k} - \frac{u_{out,g}}{m_g} x_{in,g,k}, & x_{in,g,k}(0) &= 0, \forall k = 1, \dots, p_g, \text{ (extents of gas inlet)} \\ \dot{\lambda}_g &= -\frac{u_{out,g}}{m_g} \lambda_g, & \lambda_g(0) &= 1, \text{ (discounting of } \mathbf{n}_{g0} \text{)} \end{aligned} \quad (3.27)$$

where $x_{m,g,j}$ is the extent of the j th mass transfer for the gas phase expressed in kg, $x_{in,g,k}$ the extent of the k th gas inlet expressed in kg, and λ_g the scalar dimensionless variable used to discount the effect of the initial conditions in the gas phase. The matrices $\bar{\mathbf{M}}_g$ and \mathbf{Q}_g are computed using the algorithm given in Appendix C. The numbers of moles $\mathbf{n}_g(t)$ can be expressed in terms of the extents $\mathbf{x}_{m,g}(t)$, $\mathbf{x}_{in,g}(t)$ and the discounting variable $\lambda_g(t)$ as follows:

$$\mathbf{n}_g(t) = -\mathbf{W}_{m,g} \mathbf{x}_{m,g}(t) + \mathbf{W}_{in,g} \mathbf{x}_{in,g}(t) + \mathbf{n}_{g0} \lambda_g(t). \quad (3.28)$$

(Proof follows from Theorem 2.2)

Remarks

1. It is convenient to express the transformed system completely in terms of extents by introducing the dimensionless scalar extent of gas outlet $x_{out,g}(t) = 1 - \lambda_g(t)$, with which Eq. (3.28) becomes:

$$\mathbf{n}_g(t) = \mathbf{n}_{g0} - \mathbf{W}_{m,g} \mathbf{x}_{m,g}(t) + \mathbf{W}_{in,g} \mathbf{x}_{in,g}(t) - \mathbf{n}_{g0} x_{out,g}(t). \quad (3.29)$$

2. Transformation (3.25) requires the knowledge of $\bar{\mathbf{W}}_{in,g}$, and \mathbf{n}_{g0} . It depends on the initial conditions \mathbf{n}_{g0} .
3. The transformed reaction system for the gas phase is of dimension $(\bar{p}_g + 1)$. The $(S_g - \bar{p}_g)$ invariant states $\mathbf{x}_{iv,g}(t)$ are identically equal to zero as follows and can be discarded:

$$\mathbf{x}_{iv,g}(t) = \mathbf{Q}_{g0}^T \mathbf{n}_g(t) = \mathbf{0}_{S_g - \bar{p}_g}, \quad (3.30)$$

Here, note that $\text{rank}(\mathbf{Q}_{g0}) = S_g - \bar{p}_g - 1$.

The interpretation of the extents $\mathbf{x}_{m,g}$, $\mathbf{x}_{in,g}$ and $x_{out,g}$ is given next.

Extents of mass transfer $\mathbf{x}_{m,g}$ [kg].

For a species transferring from the gas to the liquid, the extent of mass transfer $x_{m,g,j}$ ($\forall j = 1, \dots, p_{gl}$) is positive and corresponds to the mass of that species that would have accumulated and remained in the gas phase had there not been any mass transfer. For a species transferring from the liquid to the gas, the extent of mass transfer $x_{m,g,j}$ ($\forall j = p_{gl} + 1, \dots, p_m$) is negative, with its absolute value corresponding to the mass transferred to the gas that is still in the reactor.

Extents of gas inlet $\mathbf{x}_{in,g}$ [kg]

The extent of gas inlet $x_{in,g,k}$ ($\forall k = 1, \dots, p_g$) is the mass added by the k th gas inlet that remains in the reactor. The term $-\frac{u_{out,g}}{m_g} x_{in,g,k}$ accounts for the material added by the k th gas inlet that is removed from the gas phase through the gas outlet.

Extent of gas outlet $x_{out,g}$ [–]

The extent of gas outlet $x_{out,g}(t) = 1 - \lambda_g(t)$ is the fraction of \mathbf{n}_{g0} that has been removed through the gas outlet. Without gas outlet, $\lambda_g(t) = 1$ and $x_{out,g}(t) = 0$.

3.2.3 Special case: Gas–liquid reactor without outlet

A particular situation arises when there is no outlet, as in batch and semi-batch reactors. In such a case, the gas and liquid phases can be treated simultaneously by combining Eqs. (3.15)-(3.16) to give:

$$\dot{\mathbf{n}}(t) = \bar{\mathbf{N}}^T V_l(t) \mathbf{r}(t) + \bar{\mathbf{W}}_{in} \bar{\mathbf{u}}_{in}(t), \quad \mathbf{n}(0) = \mathbf{n}_0, \quad (3.31)$$

where $\mathbf{n} = \begin{bmatrix} \mathbf{n}_g \\ \mathbf{n}_l \end{bmatrix}$ is the S -dimensional vector of numbers of moles in the two phases,

$S = S_g + S_l$, $\bar{\mathbf{N}} = \begin{bmatrix} \mathbf{0}_{R \times S_g} & \mathbf{N} \end{bmatrix}$ the $R \times S$ stoichiometric matrix, $\bar{\mathbf{u}}_{in} = \begin{bmatrix} \mathbf{u}_{in,g} \\ \mathbf{u}_{in,l} \\ \boldsymbol{\zeta} \end{bmatrix}$

the \bar{p} -dimensional vector of inlet and mass-transfer rates, with $\bar{p} = p_g + p_l + p_m$,

$\bar{\mathbf{W}}_{in} = \begin{bmatrix} \tilde{\mathbf{W}}_{in,g} & \tilde{\mathbf{W}}_{in,l} & \mathbf{W}_m \end{bmatrix} = \begin{bmatrix} \mathbf{W}_{in,g} & \mathbf{0}_{S_g \times p_g} & -\mathbf{W}_{m,g} \\ \mathbf{0}_{S_l \times p_l} & \mathbf{W}_{in,l} & \mathbf{W}_{m,l} \end{bmatrix}$ the extended-inlet matrix.

Eq. (3.31) resembles Eq. (3.16) with $u_{out,l} = 0$. Hence, the transformation of Theorem 3.1 applies directly to Eq. (3.31) and gives the following extents:

$$\begin{aligned} \dot{x}_{r,i} &= V_l r_i, & x_{r,i}(0) &= 0, \quad \forall i = 1, \dots, R, & (\text{extents of reaction}) \\ \dot{x}_{m,j} &= \zeta_j, & x_{m,j}(0) &= 0, \quad \forall j = 1, \dots, p_m, & (\text{extents of mass transfer}) \\ \dot{x}_{in,l,k} &= u_{in,l,k}, & x_{in,l,k}(0) &= 0, \quad \forall k = 1, \dots, p_l, & (\text{extents of liquid inlet}) \\ \dot{x}_{in,g,k} &= u_{in,g,k}, & x_{in,g,k}(0) &= 0, \quad \forall k = 1, \dots, p_g. & (\text{extents of gas inlet}) \end{aligned} \quad (3.32)$$

The numbers of moles $\mathbf{n}(t)$ in the gas and liquid phases can be expressed in terms of extents as follows:

$$\mathbf{n}(t) = \mathbf{n}_0 + \bar{\mathbf{N}}^T \mathbf{x}_r(t) + \mathbf{W}_m \mathbf{x}_m(t) + \tilde{\mathbf{W}}_{in,l} \mathbf{x}_{in,l}(t) + \tilde{\mathbf{W}}_{in,g} \mathbf{x}_{in,g}(t). \quad (3.33)$$

Remarks

1. The transformed space is of dimension $R + \bar{p}$. The $S - R - \bar{p}$ invariant states \mathbf{x}_{iv} are identically equal to zero and can be discarded.
2. The element $x_{r,i}$ can be interpreted as the extent of the i th reaction, $x_{m,j}$ the extent of the j th mass transfer, $x_{in,l,k}$ the extent of the k th liquid inlet, and $x_{in,g,k}$ the extent of the k th gas inlet. Note that, without outlet, the extents of mass transfer \mathbf{x}_m are the same for both phases.

3.2.4 Extension to unsteady-state mass-transfer models

Model (3.9)-(3.10) assumes that there is neither accumulation nor reaction in the boundary layer. However, mass-transfer phenomena are often more accurately described by unsteady-state mass-transfer models governed by partial differential equations [66, 67, 91, 92]:

$$F_s \left(\partial c_{s,f} / \partial t, \nabla c_{s,f}, \nabla^2 c_{s,f} \right) = 0 \quad \text{with} \quad (\text{B.C})_{s,f}, \quad (\text{I.C.})_{s,f}, \quad (3.34)$$

$$s \in \mathcal{S}_m, \quad f \in \{g, l\},$$

where F_s is a function of (i) the accumulation of the s th species in the f phase film expressed by the time derivative $\partial c_{s,f}/\partial t$, (ii) convection expressed by the first spatial derivative $\nabla c_{s,f}$, and (iii) diffusion expressed by the second spatial derivative $\nabla^2 c_{s,f}$. $(\text{B.C.})_{s,f}$ and $(\text{I.C.})_{s,f}$ are the boundary and initial conditions for the s th species in the f phase, respectively.

Since the transferring species accumulate in the gas and liquid films during unsteady-state mass transfer, the overall mass–transfer rate vector ζ in Eqs. (3.9)–(3.10) is replaced by the p_m -dimensional mass–transfer rates ζ_g and ζ_l for the gas and liquid phases, respectively, to give:

Gas phase

$$\dot{\mathbf{n}}_g(t) = \mathbf{W}_{in,g} \mathbf{u}_{in,g}(t) - \mathbf{W}_{m,g} \zeta_g(t) - \frac{u_{out,g}(t)}{m_g(t)} \mathbf{n}_g(t), \quad \mathbf{n}_g(0) = \mathbf{n}_{g0} \text{ with } \zeta_g = \begin{bmatrix} \zeta_{g^l} \\ -\zeta_{lg} \end{bmatrix}_g, \quad (3.35)$$

Liquid phase

$$\begin{aligned} \dot{\mathbf{n}}_l(t) &= \mathbf{N}^T V_l(t) \mathbf{r}(t) + \mathbf{W}_{in,l} \mathbf{u}_{in,l}(t) + \mathbf{W}_{m,l} \zeta_l(t) - \frac{u_{out,l}(t)}{m_l(t)} \mathbf{n}_l(t), \quad \mathbf{n}_l(0) = \mathbf{n}_{l0}, \\ \text{with } \zeta_l &= \begin{bmatrix} \zeta_{l^l} \\ -\zeta_{lg} \end{bmatrix}_l. \end{aligned} \quad (3.36)$$

ζ_g and ζ_l are obtained by solving Eq. (3.34), the boundary conditions of which are functions of the bulk concentrations given by Eqs. (3.35) and (3.36). Hence, Eqs. (3.34)–(3.36) need to be solved simultaneously.

The transformations in Theorem 3.1 and Corollary 3.1 compute the extents of reaction, mass–transfer and flow using information regarding only the stoichiometry, the inlet and mass–transfer matrices and the initial conditions in the bulk phases. Upon replacing ζ_b ($\forall j = 1, \dots, p_m$) by $\zeta_{g,j}$ and $\zeta_{l,j}$, the transformations in Theorem 3.1 and Corollary 3.1 hold also for unsteady-state mass transfer.

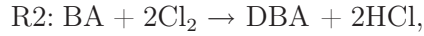
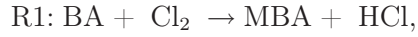
Note that, for the case of G–L reactors without outlet and with unsteady-state mass transfer, \mathbf{n}_g and \mathbf{n}_l cannot be combined and treated simultaneously due to the presence of the mass–transfer rates $\zeta_{g,j}$ and $\zeta_{l,j}$ instead of simply ζ_j .

3.3 Illustrative simulated example

The implication of being able to compute the extents of reaction, mass–transfer and flow from measured data is illustrated through the isothermal, varying-density G–L reaction system involving the chlorination of butanoic acid. Chlorinated carboxylic acids are important intermediary products, for example in the production of pharmaceuticals, dyes and herbicides.

Reaction system

The chlorination of butanoic acid (BA) takes place in the organic liquid phase with ethanol as solvent and it involves two parallel auto-catalytic reactions that consume dissolved Cl_2 . The main reaction produces the desired product α -monochlorobutanoic acid (MBA) and hydrochloric acid (HCl). The second reaction produces the side product α -dichlorobutanoic acid (DBA) and HCl. HCl is a highly volatile product that is found in both phases [101]. The reaction stoichiometry reads:



with the kinetic expressions:

$$\begin{aligned} r_1 &= \frac{k_1 \sqrt{c_{\text{MBA}}} + k_2}{1 + k_3 c_{\text{Cl}_2}} \left(\frac{c_{\text{BA}}}{c_{\text{BA}} + \epsilon_1} \right) \left(\frac{c_{\text{Cl}_2}}{c_{\text{Cl}_2} + \epsilon_2} \right) \\ r_2 &= k_4 r_1 c_{\text{Cl}_2}. \end{aligned} \quad (3.37)$$

The kinetic and thermodynamic parameters are given in Table 3.1 [68]. Mass-transfer rates (in kg s^{-1}) are calculated using the following equations:

$$\begin{aligned} \zeta_{gl, \text{Cl}_2} &= k_{\text{Cl}_2} A V_l M_{w, \text{Cl}_2} (c_{\text{Cl}_2}^* - c_{\text{Cl}_2}), \\ \zeta_{lg, \text{HCl}} &= k_{\text{HCl}} A V_l M_{w, \text{HCl}} (c_{\text{HCl}} - c_{\text{HCl}}^*), \end{aligned} \quad (3.38)$$

where $c_{\text{Cl}_2}^*$ and c_{HCl}^* are the equilibrium molar concentrations of Cl_2 and HCl at the interface and c_{Cl_2} and c_{HCl} are the molar concentrations of Cl_2 and HCl in the bulk, respectively. The equilibrium concentrations are calculated using Henry's law given by Eq. (3.4). The partial pressures in the gas phase are calculated using the ideal gas law.

Three cases are considered, each with a different type of reactor, namely with (i) gas inlet and no outlet, (ii) gas inlet and gas outlet, and (iii) both gas and liquid inlets and outlets. The details regarding the numbers of species, independent reactions, mass transfers, and inlet and outlet flows are given in Table 3.2. The reactions take place in the solvent (ethanol) and the total reactor volume is 9 m^3 .

3.3.1 Case 1: Reactor with gas inlet and no outlet

Simulation to generate the numbers of moles:

In Case 1, 100 kmol of ethanol, 13 kmol of BA and a small amount of MBA as catalyst (10^{-5} kmol) are placed in the reactor. The gas phase contains initially air at atmospheric pressure (1 bar). Then, Cl_2 is fed continuously for 1 h with the mass flowrate 972 kg h^{-1} . The initial volumes of the liquid and gas phases are 7.156 m^3 and 1.844 m^3 , respectively. The reaction system has two gaseous species ($\mathcal{S}_g = \{\text{Cl}_2, \text{HCl}\}$, $S_g = 2$),

Table 3.1 Thermodynamics, hydrodynamics and kinetic parameters

Kinetic Parameters	$k_1 = 0.045632e^{(5.76-3260/T)}\alpha^{0.5} [(\text{kmol m}^{-3})^{1/2}\text{s}^{-1}]$ $k_2 = 0.475783e^{(5.34-3760/T)}\alpha [\text{kmol m}^{-3} \text{s}^{-1}]$ $k_3 = 1.3577 [\text{m}^3 \text{kmol}^{-1}]$ $k_4 = 0.1$ $\epsilon_1 = 0.2$ $\epsilon_2 = 1$
Catalyst mole fraction $\alpha = 0.037$	
Thermodynamic data	Henry constants, $H_{c,Cl_2} = H_{c,HCl} = 70.33 [\text{bar m}^3 \text{kmol}^{-1}]$ Molecular weights $[\text{kg kmol}^{-1}]$: $M_{w,BA} = 88.12$ $M_{w,MBA} = 122.52$ $M_{w,DBA} = 156.97$ $M_{w,Cl_2} = 71$ $M_{w,HCl} = 36.45$ $M_{w,EtOH} = 46$ Liquid densities of pure species $[\text{kg m}^{-3}]$: $\rho_{l,BA} = 859.17$ $\rho_{l,MBA} = 1085.53$ $\rho_{l,DBA} = 1070$ $\rho_{l,Cl_2} = 1093$ $\rho_{l,HCl} = 1486.26$ $\rho_{l,EtOH} = 790$
Hydrodynamic data	Specific interfacial area $A = 254.9 [\text{m}^{-1}]$: Molar transfer coefficients: $[\text{m s}^{-1}]$ $k_{Cl_2} = 0.666 \times 10^{-4}$ $k_{HCl} = 0.845 \times 10^{-4}$

Table 3.2 Numbers of species S_l and S_g , independent reactions R , mass transfers p_m , inlet flows p_l and p_g , and liquid and gas outlets for the three cases studied.

Case No.	S_l	S_g	R	p_m	p_l	p_g	Liquid outlet	Gas outlet
1 (gas inlet, no outlet)	5	2	2	2	0	1	0	0
2 (gas inlet and gas outlet)	5	3	2	2	0	1	0	1
3 (gas and liquid inlets and outlets)	6	3	2	2	1	1	1	1

five liquid-phase species ($\mathcal{S}_l = \{\text{Cl}_2, \text{BA}, \text{MBA}, \text{HCl}, \text{DBA}\}^1$, $S_l = 5$), two reactions (R1 and R2, $R = 2$), one gas inlet (Cl_2 , $p_g = 1$ and $p_l = 0$), and two transferring species ($\mathcal{S}_{gl} = \{\text{Cl}_2\}$, $\mathcal{S}_{lg} = \{\text{HCl}\}$, $S_m = S_{gl} + S_{lg} = 1 + 1 = 2$). Since there is no outlet, the mole balance equations for the gas and liquid phases can be combined as in Eq. (3.31), with $S = 7$ and $\mathbf{n} = [n_{\text{Cl}_{2,g}} \ n_{\text{HCl}_g} \vdots n_{\text{Cl}_{2,l}} \ n_{\text{BA}_l} \ n_{\text{MBA}_l} \ n_{\text{HCl}_l} \ n_{\text{DBA}_l}]^T$. The initial conditions are: $\mathbf{n}_0 = [0 \ 0 \vdots 0 \ 13 \ 10^{-6} \ 0 \ 0]^T$ kmol, $m_{l0} = 5523$ kg. The stoichiometric and extended-inlet matrices are:

$$\bar{\mathbf{N}} = [\mathbf{0}_{2 \times 2} \vdots \mathbf{N}] = \begin{bmatrix} 0 & 0 & \vdots & -1 & -1 & 1 & 1 & 0 \\ 0 & 0 & \vdots & -2 & -1 & 0 & 2 & 1 \end{bmatrix}; \quad (3.39)$$

$$\bar{\mathbf{W}}_{in} = \begin{bmatrix} \mathbf{w}_{in,g} & \vdots & -\mathbf{w}_{m,g} \\ \cdots & \cdots & \cdots \\ \mathbf{0}_{5 \times 1} & \vdots & \mathbf{w}_{m,l} \end{bmatrix} = \begin{bmatrix} 0.0141 & \vdots & -0.0141 & 0 \\ 0 & \vdots & 0 & -0.0274 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & \vdots & 0.0141 & 0 \\ 0 & \vdots & 0 & 0 \\ 0 & \vdots & 0 & 0 \\ 0 & \vdots & 0 & 0.0274 \\ 0 & \vdots & 0 & 0 \end{bmatrix}. \quad (3.40)$$

The liquid density is calculated as:

$$\rho_l = \frac{1}{\sum_{s=1}^{S_l} \frac{S_l}{\rho_{l,s}} y_{w,s}}, \quad (3.41)$$

where $y_{w,s}$ is the weight fraction of the s th species in the liquid phase and $\rho_{l,s}$ is the corresponding pure liquid density assumed to be constant.

The numbers of moles in the liquid phase and the partial pressures in the gas phase are simulated using Eqs. (3.15) and (3.16) and are considered as noise-free measured data (see Figure 3.4). With no outlet and a constant reactor volume, the partial pressure of HCl, which is produced by both reactions, increases with time. Note that the partial pressure of Cl_2 remains nearly constant, an indication that the Cl_2 fed to the reactor transfers immediately to the liquid phase.

Computed extents:

The extents of reaction, mass transfer and gas inlet are computed using the transformation of Theorem 3.1 applied to the measured vector $\mathbf{n}(t)$, i.e. without information regarding kinetics and mass-transfer rates. Figure 3.5a shows the extents of reaction, with $x_{r,1}$ and $x_{r,2}$ corresponding to the numbers of moles converted by reactions R1 and R2, respectively. BA is the limiting reactant that is consumed by both reactions R1

¹ Note that the solvent ethanol, which neither reacts nor leaves the reactor, does not need be accounted for.

and R2. Because MBA is produced by reaction R1 only, $x_{r,1}$ also represents the number of moles of MBA produced and approaches steady state, indicating the completion of reaction R1. Similarly, since DBA is produced by R2 only, $x_{r,2}$ indicates the number of moles of DBA and also approaches steady state, indicating the completion of R2. Since reactions R1 and R2 are autocatalytic, they start slowly due to small amount of MBA present initially in the reactor. This leads to an accumulation of Cl_2 in the liquid phase (see Figure 3.4a). After about 0.25 h, the rates of both reactions increase, which leaves only small amounts of Cl_2 in the liquid phase. Since the rate r_2 is proportional to c_{l,Cl_2}^2 , it is very small after 0.25 h, which results in a nearly constant $x_{r,2}$ value. Both reactions stop upon total consumption of BA after about 0.9 h.

Figure 3.5b shows the extents of inlet flow $x_{in,g}$ and mass transfer \mathbf{x}_m , where $x_{in,g}$ corresponds to the amount of Cl_2 fed to the gas phase, $x_{m,1}$ and $x_{m,2}$ to the amounts of Cl_2 and HCl transferred from the gas phase to the liquid phase, respectively. Note that $x_{m,2}$ is negative since HCl transfers from the liquid to the gas. Note also that, without outlet, the two extents of mass transfer are the same for the gas and liquid phases. $x_{in,g}$ increases with time due to the continuous feeding of Cl_2 . Since Cl_2 is fed into the gas phase and is consumed in the liquid phase, $x_{m,1}$ increases with time, while $x_{m,2}$ decreases due to production of HCl in the liquid phase and its transfer to the gas phase. Once the consumption of Cl_2 and the production of HCl stop following the complete consumption of BA after 0.9 h, the transfer of Cl_2 slows down since the liquid phase becomes saturated with Cl_2 , while that of HCl stops. Since Cl_2 is fed continuously to the gas phase and consumed rapidly in the liquid phase, $x_{m,1} \simeq x_{in,g}$ until complete consumption of BA.

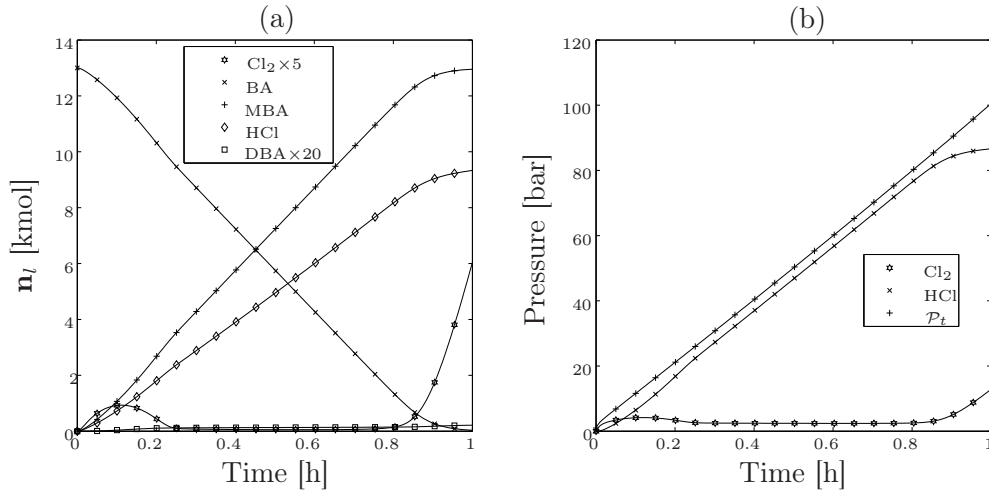


Figure 3.4 Case 1: Reactor with a gas inlet and no outlet. Time profiles of (a) the numbers of moles in the liquid phase, and (b) the partial and total (\mathcal{P}_t) pressures in the gas phase.

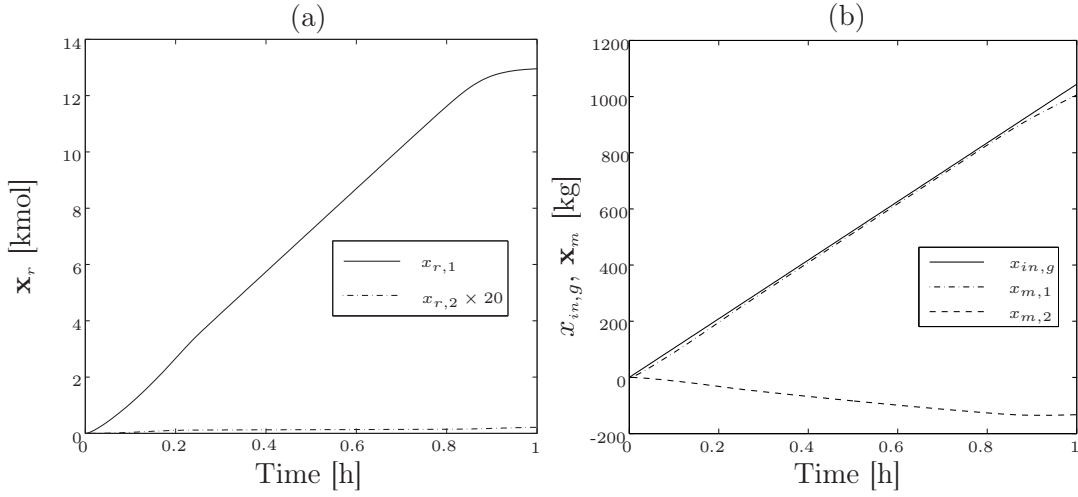


Figure 3.5 Case 1: Reactor with a gas inlet and no outlet. Time profiles of (a) the extents of reaction x_r , and (b) the extents of inlet flow $x_{in,g}$ and of mass transfer x_m .

3.3.2 Case 2: Reactor with gas inlet and gas outlet

Simulation to generate the numbers of moles:

The gas phase has one inlet ($p_g = 1$) and one outlet. Due to the presence of the outlet, the liquid and gas phases need to be handled separately.

Initially, 13 kmol of BA and 100 kmol of ethanol as solvent are present in the reactor. The gas phase contains only air at atmospheric pressure (1 bar). Since air is removed with the outlet, the mole balance of air needs to be considered, thus $S_g = 3$ with $\mathbf{S}_g = \{air, Cl_2, HCl\}$. The initial numbers of moles in the gas phase is $\mathbf{n}_{g0} = [0.054 \ 0 \ 0]^T$ kmol. Furthermore, $S_l = 5$ with $\mathbf{S}_l = \{Cl_2, BA, MBA, HCl, DBA\}^2$. The initial numbers of moles in the liquid phase is $\mathbf{n}_{l0} = [0 \ 13 \ 0 \ 0 \ 0]^T$. The initial volumes of the liquid and gas phases are 7.156 m³ and 1.844 m³, respectively. It is desired to maintain the pressure at 10 bar, for which a constant gas outlet of 511.2 kg h⁻¹ and a varying inlet flow of Cl₂ are used.

The stoichiometric matrix and extended inlet matrices for the gas and liquid phases read:

$$\mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 0 & 1 \\ -2 & -1 & 0 & 2 & 1 \end{bmatrix}; \quad \bar{\mathbf{W}}_{in,g} = \begin{bmatrix} 0 & 0 & 0 \\ 0.0141 & -0.0141 & 0 \\ 0 & 0 & -0.0274 \end{bmatrix}; \quad \bar{\mathbf{W}}_{in,l} = \begin{bmatrix} 0.0141 & 0 \\ 0 & 0 \\ 0 & 0.0274 \\ 0 & 0 \end{bmatrix}. \quad (3.42)$$

The numbers of moles in the liquid phase and the partial pressures in the gas phase are simulated using Eqs. (3.15) and (3.16) and are considered as noise-free measured

² Since ethanol neither reacts nor leaves the reactor, it is not considered in the mole balance.

data (Figure 3.6). Figure 3.6c represents the inlet flowrate of Cl_2 that is adjusted by PID control to maintain the total pressure in the reactor at 10 bar.

Computed extents:

Since $\text{rank}(\bar{\mathbf{W}}_{in,g}) = 2 < \bar{p}_g = 3$, the assumption $\text{rank}(\bar{\mathbf{W}}_{in,g}, \mathbf{n}_{g0}) = \bar{p}_g + 1 = 4$ needed in Corollary 3.1 does not hold, and thus the extents of inlet and mass transfer for the gas phase cannot be computed from \mathbf{n}_g . However, for the liquid phase, the extents of reaction \mathbf{x}_r and of mass transfer $\mathbf{x}_{m,l}$ can be computed and are shown in Figure 3.7. Again, the extents of reaction $x_{r,1}$ and $x_{r,2}$ correspond to the numbers of moles of MBA and DBA, respectively. Initially, the transfer rate of Cl_2 to the liquid phase, as given by the slope of $x_{m,l,1}$, is important due to the high partial pressure of Cl_2 , then it reduces with the decrease in Cl_2 partial pressure. $x_{m,l,2}$ increases steadily in magnitude as HCl is continuously produced in the liquid phase and transfers to the gas phase.

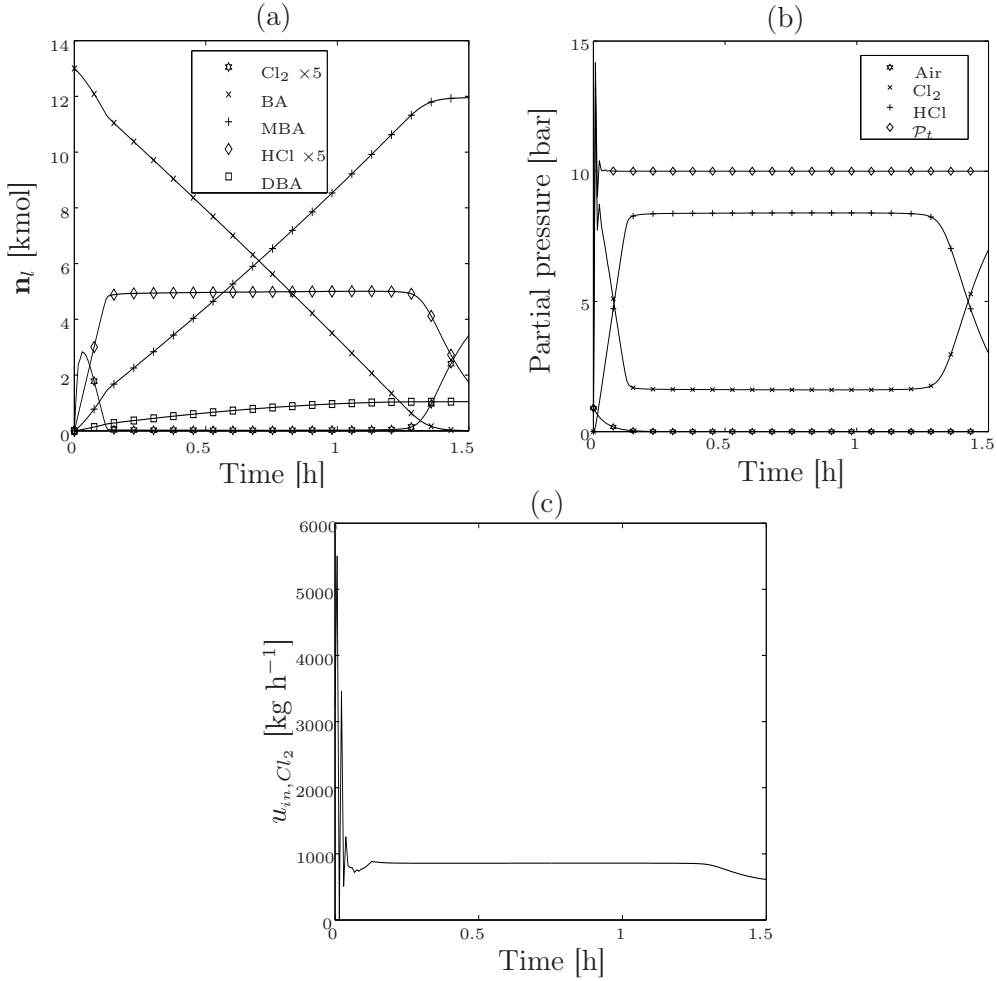


Figure 3.6 Case 2: Reactor with gas inlet and gas outlet. Time profiles of (a) the numbers of moles in the liquid phase, (b) the partial and total (\mathcal{P}_t) pressures in the gas phase, and (c) the inlet flowrate of Cl_2 .

3.3.3 Case 3: Reactor with gas and liquid inlets and outlets

Simulation to generate the numbers of moles:

Compared to Case 2, the liquid phase is considered to be a CSTR with the inlet $u_{in,l}$ and the outlet $u_{out,l}$ computed according to Eq. (3.14), hence $p_g = p_l = 1$.

Initially, 100 kmol of ethanol are charged in the reactor. The gas phase contains only air at atmospheric pressure (1 bar). The gas phase is then raised and maintained at 10 bar by feeding Cl_2 with a constant gas outlet of 27 kg h $^{-1}$. BA is fed for 5 h to the liquid phase with the mass flowrate 324 kg h $^{-1}$. The mole balance for the solvent (ethanol) needs to be taken into account since its amount in the reactor changes due to the liquid outlet, which affects the mixture density; however, it does not take part in the reactions. Hence, $S_l = 6$ with $\mathcal{S}_l = \{\text{Cl}_2, \text{BA}, \text{MBA}, \text{HCl}, \text{DBA}, \text{Ethanol}\}$ and

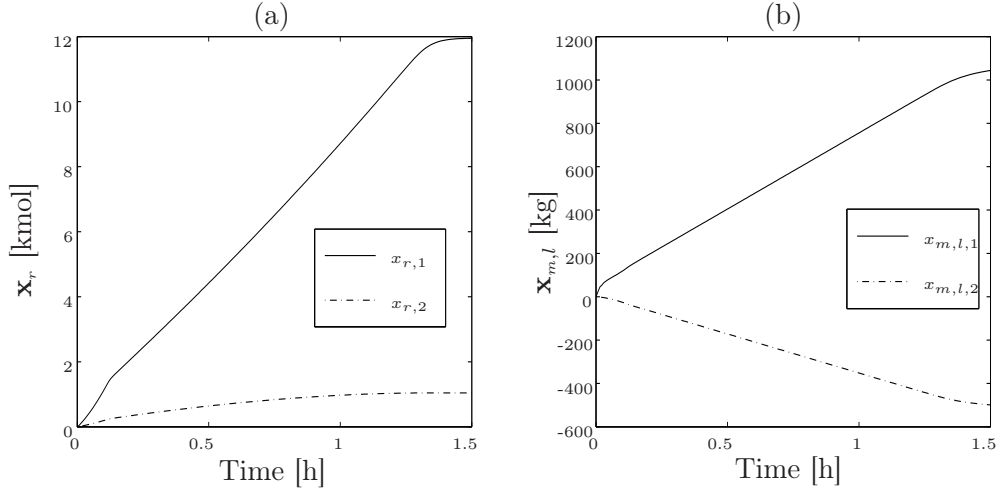


Figure 3.7 Case 2: Reactor with gas inlet and gas outlet. Time profiles of (a) the extents of reaction \mathbf{x}_r , and (b) the extents of mass transfer $\mathbf{x}_{m,l}$.

$S_g = 3$ with $\mathcal{S}_g = \{\text{air}, \text{Cl}_2, \text{HCl}\}$. The initial numbers of moles in the liquid phase is $\mathbf{n}_{l0} = [0 \ 0 \ 0 \ 0 \ 0 \ 100]^\top$ kmol. The initial volumes of the gas and liquid phases are 3.177 m^3 and 5.823 m^3 , respectively.

The extended-inlet matrix $\bar{\mathbf{W}}_{in,g}$ for the gas phase is identical to that in Case 2. The stoichiometric and inlet matrices for the liquid phase read:

$$\mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 0 & 1 & 0 \\ -2 & -1 & 0 & 2 & 1 & 0 \end{bmatrix}; \quad \bar{\mathbf{W}}_{in,l} = \begin{bmatrix} 0 & 0.0141 & 0 \\ 0.0113 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0.02740 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \quad (3.43)$$

The numbers of moles in the liquid phase and the partial pressures in the gas phase are simulated using Eqs. (3.15) and (3.16) and are considered as noise-free measured data (see Figure 3.8). The inlet flowrate of Cl_2 is shown in Figure 3.8c.

Computed extents:

Similar to Case 2, the extents of inlet and mass transfer for the gas phase cannot be computed since $\text{rank}(\bar{\mathbf{W}}_{in,g}) < \bar{p}_g$. The extents for the liquid phase, which are computed using Eq. (3.17), are shown in Figure 3.9 and discussed next.

Extents of reaction

Figure 3.9a shows the extents of reaction $x_{r,1}$ and $x_{r,2}$ corresponding to reactions R1 and R2. A comparison with Figure 3.8a shows that the extents of reaction indeed correspond to the numbers of moles of MBA and DBA that remain in the reactor. Since Cl_2 transfers continuously from the gas to the liquid, and BA is also fed continuously, the extents $x_{r,1}$ and $x_{r,2}$ increase with time.

Extents of mass transfer

Figure 3.9b shows the extents of mass transfer $x_{m,l,1}$ and $x_{m,l,2}$ corresponding to the transfers of Cl_2 and HCl . $x_{m,l,1}$ increases rapidly initially due to the large driving force Δc_{Cl_2} . In contrast, the mass transfer of HCl from the liquid to the gas $x_{m,l,2}$ is highly correlated with the extents of reaction since HCl is produced by both reactions.

Extents of liquid inlet

Figure 3.9b also shows the extent of liquid inlet $x_{in,l}$. BA is fed at a constant rate, and $x_{in,l}$ increases steadily. However, it is not exactly a linear increase with a constant slope since $x_{in,l}$ only accounts for the amount of BA fed that remains in the reactor.

Extent of liquid outlet

Figure 3.9c shows the extent of liquid outlet $x_{out,l}$, which indicates the fraction of initial liquid (ethanol) that has left the reactor at time t through the liquid outlet. It is seen that 38% of the initial amount of ethanol has been removed from the reactor after 5 h.

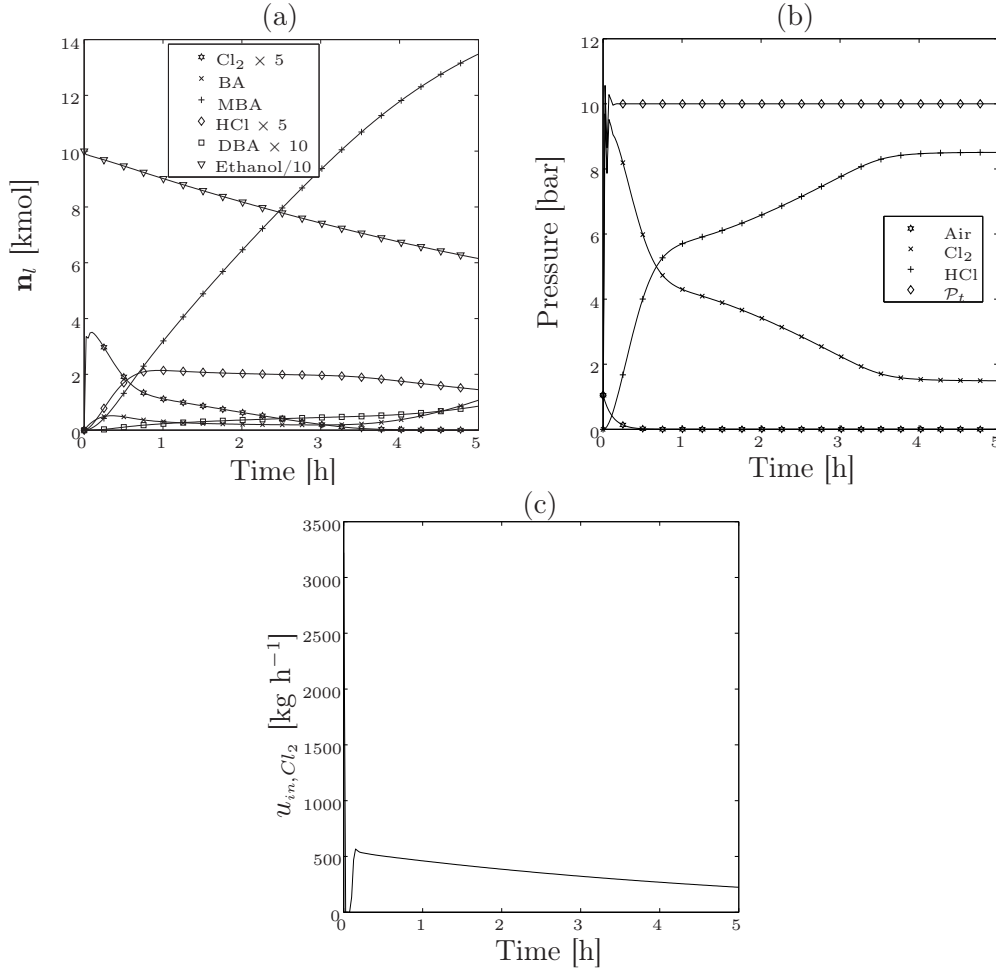


Figure 3.8 Case 3: Reactor with both gas and liquid inlets and outlets. Time profiles of (a) the numbers of moles in the liquid phase, (b) the partial and total (P_t) pressures in the gas phase, and (c) the inlet flowrate of Cl_2 .

3.4 Summary

This chapter has extended the concept of extents of reaction and flow, and invariants for homogeneous reaction systems to G–L reaction systems. The numbers of moles in both phases have been transformed linearly into extents of reaction, mass transfer, inlet flow and outlet flow, and invariants. For each phase, the novel concept of extent of mass transfer describes the amount of material transferred between phases that is still in the corresponding phase. It has also been shown that, for a reactor without outlet such as a batch or semi-batch reactor, the gas and liquid phases could be combined and treated simultaneously.

The proposed linear transformation requires information regarding only the stoichiometry, the inlet composition, the initial conditions, and the transferring species to compute the extents of reaction, mass transfer, inlet and outlet flow from the numbers

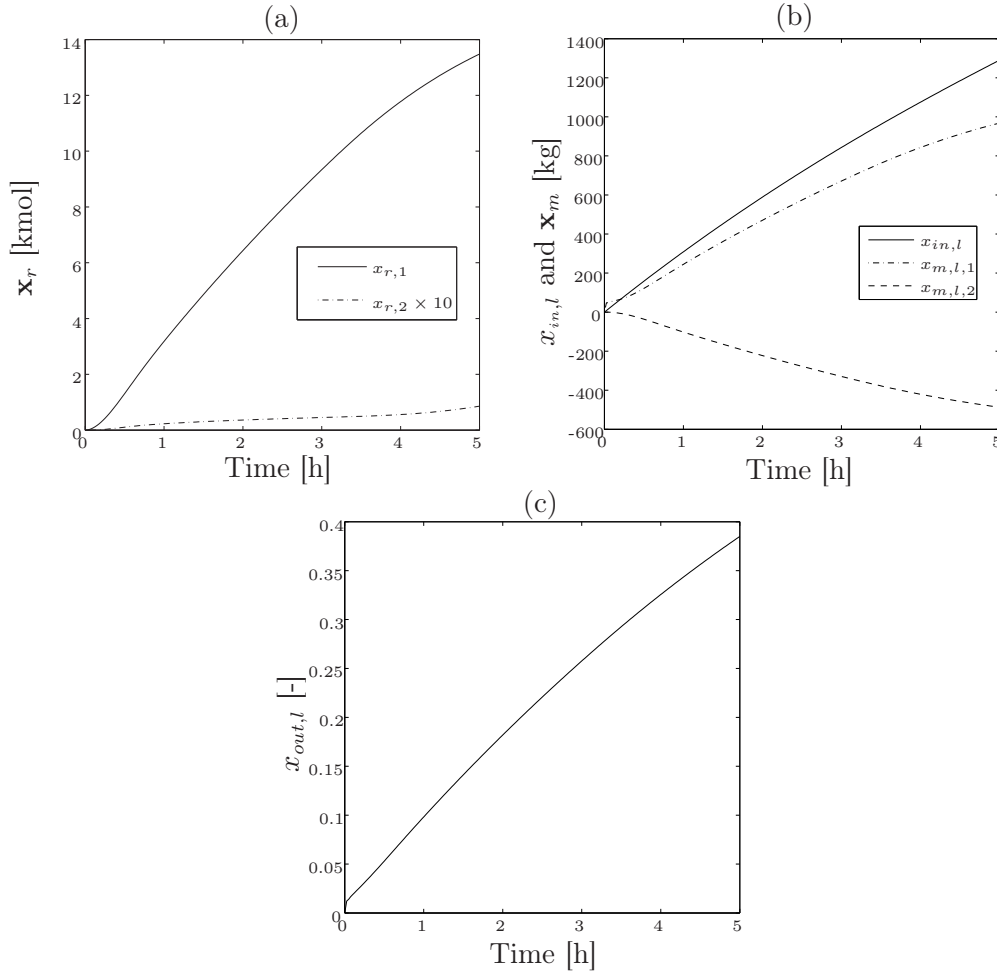


Figure 3.9 Case 3: Reactor with both gas and liquid inlets and outlets. Time profiles of (a) the extents of reaction \mathbf{x}_r , (b) the extents of liquid inlet $x_{in,l}$ and mass transfer $\mathbf{x}_{m,l}$, and (c) the extent of liquid outlet $x_{out,l}$.

of moles (Figure 3.10). Note that the typically unknown specificities regarding the kinetics, the mass-transfer rates, the energy balance and the constitutive equations (for representing densities and partial pressures) do not play any role in the transformation, which therefore fully holds for complex nonisothermal reactors. Furthermore, since the mass-transfer model of the two-film theory can also be used to describe liquid-liquid reaction systems [47, 98], the proposed transformation can also be applied to these systems. Although this work has considered G–L reactors with reactions only in the liquid phase, the proposed transformation can be extended to the case where the reactions occur in both phases.

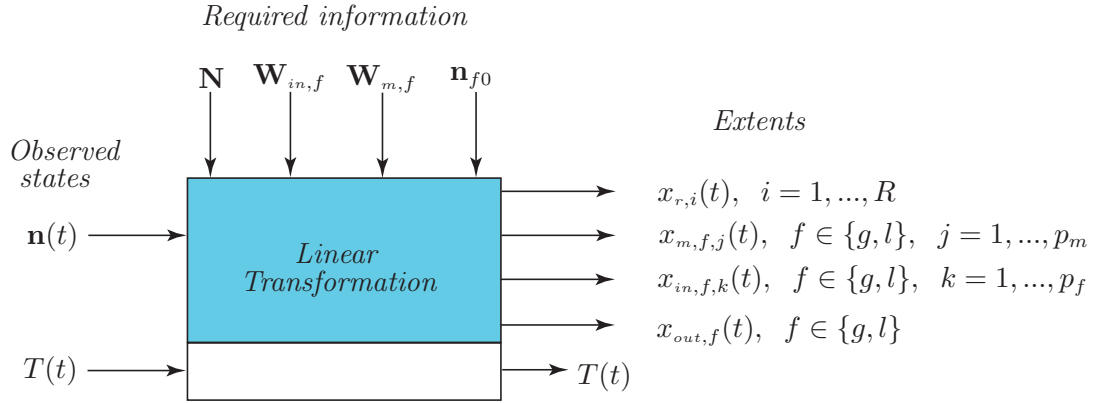


Figure 3.10 Schematic of the linear transformation to compute the various extents from the numbers of moles. The transformation is based on the stoichiometric matrix \mathbf{N} , the inlet matrix $\mathbf{W}_{in,f}$, the mass-transfer matrix $\mathbf{W}_{m,f}$, and the initial conditions \mathbf{n}_{f0} for the f phase, $f \in \{g, l\}$. Note that the transformation can be performed independently of the energy balance, kinetic and mass-transfer rate information.

Chapter 4

Minimal state representation of reaction systems

First-principles models can have a large number of states to describe the various dynamics, possibly on different time scales. However, there can be several either redundant or negligible dynamic elements in these models. A minimal state representation is a dynamic model with no redundant states¹. Such reduced-order representations simplify the dynamic model and can provide deeper insight into the reaction system [42, 60].

In practice, measurements are used for online monitoring, control and optimization of reaction systems. However, it is not possible to measure the concentrations of all the species because of limitations in the current state of sensor technology. In addition, the accurate description of reaction kinetics and mass-transfer rates are often not available. In such cases, it is necessary to reconstruct the unavailable concentrations from the available measurements. Minimal state representations help identify the minimal number of states (such as number of moles, concentrations) needed to be measured so that the unavailable states can be reconstructed.

Chapters 2 and 3 have introduced transformations to convert dynamic models of homogeneous and G–L reaction systems to the extents of reaction, the extents of mass transfer, the extents of flows and invariant states, respectively. Using the concept of local state accessibility of nonlinear systems, the conditions under which the transformed models of homogeneous and G–L reaction systems are minimal state representations will be investigated in this chapter. Moreover, using the decompositions of the numbers of moles into extents and measured flowrates, one can determine the minimal number of measured concentrations (or number of moles) that are needed to reconstruct the unavailable concentrations (or number of moles) for both homogeneous and G–L reaction systems.

This chapter considers homogeneous reaction systems in Section 4.2 and G–L reaction systems in Section 4.3. Section 4.1 introduces a mathematical definition of minimal state representation and local state accessibility. Sections 4.2.1 and 4.3.1 derive the conditions under which the transformed models are minimal state representations for homogeneous and G–L reaction systems, respectively. Approaches to reconstruct the unavailable states using the minimal number of measured states using homogeneous and G–L reaction systems are proposed in Sections 4.2.2 and 4.3.2. Section 4.4 illustrates various concepts using the simulated reaction systems.

¹ A mathematical definition of minimal state representation is given later in this chapter.

4.1 Definitions

A minimal state representation contains the minimal number of states, while exhibiting the identical dynamic behavior as the original representation. For assessing the minimal nature of a given state representation in terms of the number of state variables, it is necessary to have an appropriate definition of minimal state representation [49].

4.1.1 Definition of minimal state representation

Definition 4.1 (Minimal state representation)

Consider the following class of input-affine nonlinear systems:

$$\dot{\mathbf{w}}(t) = \mathbf{f}(\mathbf{w}(t)) + \sum_{i=1}^v \mathbf{g}_i(\mathbf{w}(t))u_i(t), \quad \mathbf{w}(0) = \mathbf{w}_0, \quad (4.1)$$

where $\mathbf{w}(t) \in \mathbb{R}^S$ is the state vector and $\mathbf{u} \in \mathbb{R}^v$ is the input vector. It will be assumed that $\mathbf{f}(\mathbf{w}) : \mathbb{R}^S \rightarrow \mathbb{R}^S$ and $\mathbf{g}_i(\mathbf{w}) : \mathbb{R}^S \rightarrow \mathbb{R}^S$ are Lipschitz with respect to \mathbf{w} .

Consider the positive integer $q \leq S$ and the following two conditions:

1. Representation condition:

$$\Sigma_q : \left\{ \begin{array}{l} \text{The transformation } \Psi : \mathbb{R}^S \rightarrow \mathbb{R}^S \text{ independent of the inputs } \mathbf{u}, \\ \boldsymbol{\xi} = \Psi(\mathbf{w}), \quad \boldsymbol{\xi} = [\boldsymbol{\xi}_1^\top, \boldsymbol{\xi}_2^\top]^\top, \\ \text{transforms Eq. (4.1) to:} \\ \dot{\boldsymbol{\xi}}_1 = \tilde{\mathbf{f}}(\boldsymbol{\xi}) + \sum_{i=1}^v \tilde{\mathbf{g}}_i(\boldsymbol{\xi})u_i, \quad \boldsymbol{\xi}_1(0) = \boldsymbol{\xi}_{1,0}, \\ \boldsymbol{\xi}_2(t) = \boldsymbol{\xi}_{2,0}, \\ \text{where } \boldsymbol{\xi}_1 \in \mathbb{R}^q, \boldsymbol{\xi}_2 \in \mathbb{R}^{S-q}, \tilde{\mathbf{f}} : \mathbb{R}^S \rightarrow \mathbb{R}^q, \tilde{\mathbf{g}}_i(\boldsymbol{\xi}) : \mathbb{R}^S \rightarrow \mathbb{R}^q \\ \text{The back transformation } \Psi^{-1} : \mathbb{R}^S \rightarrow \mathbb{R}^S \text{ independent of the inputs } \mathbf{u}, \\ \mathbf{w} = \Psi^{-1}(\boldsymbol{\xi}), \text{ transforms Eqs. (4.3) and (4.4) back to Eq. (4.1).} \end{array} \right. \quad (4.2)$$

2. Minimality condition: There does not exist another positive integer $l < q$ such that Σ_l is satisfied.

If there exists a positive integer q that satisfies the two aforementioned conditions, then Eq. (4.3) is a minimal state representation of Eq. (4.1) and q is called the minimal order.

To satisfy the representation condition, one needs to construct a transformation Ψ of the states in Eq. (4.1) such that the original states \mathbf{w} are transformed into q variant states $\boldsymbol{\xi}_1$ evolving with time and $(S - q)$ invariants $\boldsymbol{\xi}_2$ constant with time.

To check that $\boldsymbol{\xi}_1$ satisfies the minimality condition, we will use the concept of minimal realization of nonlinear systems [76, 77, 78], which is briefly sketched next. For linear

systems, it is well known that minimal realizations are both observable and controllable [69]. 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) [78]. In contrast to observability, there is no simple extension of the concept of controllability of linear systems to nonlinear systems [41, 79]. In [76, 79], the concept of state accessibility has been introduced, which is related to controllability. As in [76], minimality according to Definition 4.1 is based on the concept of state accessibility, which is briefly reviewed in the next section.

4.1.2 Definition of local state accessibility

Consider the class of input-affine nonlinear reaction systems defined in Eq. (4.1). The definition of local state accessibility is as follows:

Definition 4.2 (Local state accessibility)

The system (4.1) is locally state accessible from $\mathbf{w}_0 \in \mathbb{R}^S$ if there exists an open neighborhood $\mathcal{O} \subseteq \mathbb{R}^S$ for which $\mathcal{W}(\mathbf{w}_0, \mathcal{U}, T) = \bar{\mathbf{w}} \in \mathcal{O}$, where $\mathcal{U}: [0, T] \rightarrow \mathbb{R}^v$ is a set of vector-valued input functions and $\mathcal{W}(\mathbf{w}_0, \mathcal{U}, t)$ denotes the solution at time t .

In other words, a system is locally state accessible if, for every initial state \mathbf{w}_0 , the set of states reachable from \mathbf{w}_0 has a nonempty interior in the state space [79]. Let us define the accessibility distribution as the span of the Lie algebra that contains the set of vector fields \mathbf{f} , \mathbf{g}_i , $\forall i = 1, \dots, v$ and all the repeated Lie brackets of vector fields generated by \mathbf{f} and \mathbf{g}_i . Then, the accessibility distribution (Δ_k) is defined as:

$$\Delta_k = \text{span}\{[\mathbf{f}^l, \mathbf{g}_i], 0 \leq l \leq k, 1 \leq i \leq v\}, \quad (4.5)$$

where $[\cdot, \cdot]$ indicates the Lie bracket, and $[\mathbf{f}^l, \mathbf{g}_i]$ the iterated Lie bracket of $[\mathbf{f}, [\mathbf{f}^{l-1}, \mathbf{g}_i]]$ and $[\mathbf{f}^0, \mathbf{g}_i] = \mathbf{g}_i$.

Lemma 4.1 (Bastin and Lévine [12], Sussmann and Jurdjevic [79])

If $\dim(\Delta_k(\mathbf{w})) = S$ for all $\mathbf{w} \in \mathbb{R}^S$, then the system (4.1) is locally state accessible from \mathbf{w} .

4.2 Open homogeneous reaction systems

In Chapter 2, Theorem 2.2 introduced the linear transformation of dynamic models of homogeneous reaction systems. In this section, the conditions under which the transformed model is minimal state representation will be derived. Furthermore, an approach for reconstructing the unavailable numbers of moles (or concentrations) from

the available numbers of moles (or concentrations) will be developed using the measured flowrates. Hence, this approach is labeled as *flow-based approach*.

4.2.1 Minimal state representation

Minimal state representation is proven in two parts. The first part deals with the representation condition of Definition 4.1. It will be shown that the linear transformation of Theorem 2.2 satisfies the representation condition. In the second part, the minimality condition will be proven.

Representation condition

For the linear transformation of Theorem 2.2, Ψ in Definition 4.1 is given by Eqs. (2.18) and (2.23), respectively, with the transformed states $\xi_1 = [\mathbf{x}_r^T, \mathbf{x}_{in}^T, \lambda]^T$ and $\xi_2 = \mathbf{x}_{iv}$. In addition, the inverse transformation Ψ^{-1} to reconstruct the original states \mathbf{n} from ξ is defined by Eq. (2.21). Hence, the representation condition of Definition 4.1 is fulfilled.

Since the invariant states \mathbf{x}_{iv} in Eq. (2.23) are constant, the transformed equations can be written in terms of ξ_1 as follows:

$$\dot{\xi}_1 = \begin{bmatrix} \dot{\mathbf{x}}_r \\ \dot{\mathbf{x}}_{in} \\ \dot{\lambda} \end{bmatrix} = \begin{bmatrix} \mathbf{f}_r(\xi) \\ \mathbf{0}_p \\ 0 \end{bmatrix} + \begin{bmatrix} \mathbf{0}_{R \times p} & -\frac{\mathbf{x}_r}{m} \\ \mathbf{I}_p & -\frac{\mathbf{x}_{in}}{m} \\ \mathbf{0}_{1 \times p} & -\frac{\lambda}{m} \end{bmatrix} \begin{bmatrix} \mathbf{u}_{in} \\ u_{out} \end{bmatrix}, \quad (4.6)$$

with the initial conditions $\xi_1(0) = \begin{bmatrix} \mathbf{0}_R \\ \mathbf{0}_p \\ 1 \end{bmatrix}$. ξ_1 is the $(R + v)$ -dimensional state vector,

with $v = p + \gamma$, where $\gamma = 1$ if outlet is present and $\gamma = 0$ otherwise, $\mathbf{u} = \begin{bmatrix} \mathbf{u}_{in} \\ u_{out} \end{bmatrix}$ is the v -dimensional input vector, and $\mathbf{f}_r(\xi) = V\mathbf{r}$. Hence, Eq. (4.6) is in the form of Eq. (4.3).

Minimality condition

Using results on the local state accessibility of the system (4.3), the conditions for minimal state representation of Eq. (2.1) will be proven next.

Lemma 4.2

If the system (4.3) is locally state accessible, its state dimension cannot be reduced. (See Proof in Appendix A.3)

Lemma 4.3

Consider the system (4.3) with the vector fields $\tilde{\mathbf{f}} = \begin{bmatrix} \mathbf{f}_r \\ \mathbf{0}_p \\ 0 \end{bmatrix}$ and $\tilde{\mathbf{G}} = [\tilde{\mathbf{g}}_1, \dots, \tilde{\mathbf{g}}_v] =$

$\begin{bmatrix} \mathbf{0}_{R \times p} & -\frac{\mathbf{x}_r}{m} \\ \mathbf{I}_p & -\frac{\mathbf{x}_{in}}{m} \\ \mathbf{0}_{1 \times p} & -\frac{\lambda}{m} \end{bmatrix}$. Define the matrix $\mathbf{J} = [\mathbf{f}_r \frac{\partial \mathbf{f}_r}{\partial \mathbf{x}_{in}} \frac{1}{m} (\frac{\partial \mathbf{f}_r}{\partial \mathbf{x}_r} \mathbf{x}_r + \frac{\partial \mathbf{f}_r}{\partial \mathbf{x}_{in}} \mathbf{x}_{in} + \frac{\partial \mathbf{f}_r}{\partial \lambda} \lambda - \mathbf{f}_r)]$, where the derivatives $\frac{\partial \mathbf{f}_r}{\partial \mathbf{x}_r}$, $\frac{\partial \mathbf{f}_r}{\partial \mathbf{x}_{in}}$, and $\frac{\partial \mathbf{f}_r}{\partial \lambda}$ are the sensitivities of the reaction rates \mathbf{f}_r with respect to the extents of reaction and flow (or reaction and flow variants). If $\text{rank}(\mathbf{J}) = R$, then the system is locally state accessible. (See Proof in Appendix A.4)

Using Lemmas 4.2 and 4.3, the following theorem details the conditions under which the transformed model described by Eq. (4.6) is a minimal state representation of Eq. (2.1).

Theorem 4.1 (Minimal state representation: Homogeneous reactors)

Consider the homogeneous reaction system (2.1) with $v > 0$, and define the $R \times (v+1)$ -dimensional matrix \mathbf{J} . If (i) $\text{rank}([\mathbf{N}^T \mathbf{W}_{in} \mathbf{n}_0]) = R + p + 1$ for the linear transformation of Theorem 2.2, and (ii) $\text{rank}(\mathbf{J}(t)) = R$ for some finite time interval, then the system Eq. (4.6) is a minimal state representation of Eq. (2.1). (See Proof in Appendix A.5)

Remarks.

1. $\text{rank}(\mathbf{J}(t)) = R$ is only a sufficient condition, while $\text{rank}([\mathbf{N}^T \mathbf{W}_{in} \mathbf{n}_0]) = R + p + 1$ or $\text{rank}([\mathbf{N}^T \mathbf{W}_{in}]) = R + p$ are necessary and sufficient conditions. An example illustrating the sufficient condition of $\text{rank}(\mathbf{J}(t)) = R$ is given next [75]. Consider the semi-batch reaction systems with five species ($S = 5$), three independent reactions ($R = 3$), and one inlet ($p = 1$) and assume power-law kinetics for the reaction rates. Although $\text{rank}(\mathbf{J}(t)) = 2 < 3$, it can easily be verified that the linearly transformed model is minimal state representation.
2. If $\text{rank}(\mathbf{J}(t)) < R$ and thus the accessibility distribution Δ_1 is rank deficient, i.e. $\text{rank}(\Delta_1) < R + v$, the rank of the distribution with $k > 1$ should be computed to check local accessibility.

Special reactorsSemi-batch reactors

In a semi-batch reactor, $u_{out} = 0$, $\gamma = 0$, $v = p$, and λ is constant. Then, Eq. (4.6) reduces to:

$$\dot{\xi}_1 = \begin{bmatrix} \dot{\mathbf{x}}_r \\ \dot{\mathbf{x}}_{in} \end{bmatrix} = \begin{bmatrix} \mathbf{f}_r(\xi) \\ \mathbf{0}_p \end{bmatrix} + \begin{bmatrix} \mathbf{0}_{R \times p} \\ \mathbf{I}_p \end{bmatrix} \mathbf{u}_{in}, \quad (4.7)$$

with the initial conditions $\xi_1(0) = \mathbf{0}_{R+p}$. The minimal state representation of a semi-batch reactor is of order $(R + p)$.

CSTRs

In a CSTR, $u_{out}(t)$ is computed from Eq. (2.28). The minimal state representation of a CSTR is of order $(R + p + 1)$. However, if the density is constant, $\lambda(t)$ can be computed algebraically from the states \mathbf{x}_{in} as described in Section 2.3.3. It follows that the state equation for λ can be removed from Eq. (4.6), thus leading to minimal state representation of order $(R + p)$.

4.2.2 State reconstruction

A flow-based approach for reconstructing the unavailable numbers of moles from the minimal number of available numbers of moles will be developed next using the measured flowrates. This flow-based approach proceeds in two steps: (i) the computation of extents of reaction from the available numbers of moles and the mass flowrates, and (ii) the reconstruction of the unavailable numbers of moles from the computed extents of reaction, the mass flowrates, and the initial conditions of the unavailable species.

Let $\mathbf{n}_a(t)$ be the S_a -dimensional vector of available numbers of moles at the time instant t . The subscript “a” indicates that the corresponding quantities are related to S_a available (measured) species, while the subscript “u” indicates that the corresponding quantities are related to $S_u = S - S_a$ unavailable (unmeasured) species. In addition, the inlet and outlet flowrates ($u_{in,k}(t)$, $\forall k = 1, \dots, p$ and $u_{out}(t)$) are measured at time t . The next theorem specifies the minimal number of species S_a needed to be measured in order to reconstruct the unavailable numbers of moles.

Theorem 4.2 (State reconstruction: Homogeneous reaction systems)

Let the matrices \mathbf{N} , \mathbf{W}_{in} and the initial conditions \mathbf{n}_0 be known and, without loss of generality, let \mathbf{N} and \mathbf{n} be partitioned as: $\mathbf{N} = \begin{bmatrix} \mathbf{N}_a & \mathbf{N}_u \end{bmatrix}$ and $\mathbf{n}^T = \begin{bmatrix} \mathbf{n}_a^T & \mathbf{n}_u^T \end{bmatrix}$. Furthermore, let the quantities $\mathbf{n}_a(t)$, $\mathbf{u}_{in}(t)$ and u_{out} be measured without errors. If (i) $\text{rank}(\mathbf{N}_a) = R$, then the unavailable numbers of moles $\mathbf{n}_u(t)$ can be reconstructed from the available $\mathbf{n}_a(t)$ in two steps as follows:

1. Computation of the extents of reaction $\mathbf{x}_r(t)$:

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in} - \frac{u_{out}}{m} \mathbf{x}_{in}, \quad \mathbf{x}_{in}(0) = \mathbf{0}_p, \quad (4.8)$$

$$\dot{\lambda}(t) = -\frac{u_{out}}{m} \lambda, \quad \lambda(0) = 1, \quad (4.9)$$

$$\mathbf{x}_r(t) = (\mathbf{N}_a^T)^+ (\mathbf{n}_a(t) - \mathbf{W}_{in,a} \mathbf{x}_{in}(t) - \mathbf{n}_{0,a} \lambda). \quad (4.10)$$

2. Reconstruction of the unavailable numbers of moles $\mathbf{n}_u(t)$:

$$\mathbf{n}_u(t) = \mathbf{N}_u^T \mathbf{x}_r(t) + \mathbf{W}_{in,u} \mathbf{x}_{in}(t) + \mathbf{n}_{0,u} \lambda. \quad (4.11)$$

(See Proof in Appendix A.6)

Remarks

1. The condition $\text{rank}(\mathbf{N}_a) = R$ in Theorem 4.2 specifies the minimal number of species that need to be measured, i.e. $S_a \geq R$.
2. If the concentrations of the available species \mathbf{c}_a and the volume of the reaction mixture V are available, Theorem 4.2 can be used to reconstruct the unavailable concentrations. Note that since the computation of $\mathbf{x}_r(t)$ in Eq. (4.10) is independent of the initial conditions of the unavailable species $\mathbf{n}_{0,u}$, $\mathbf{x}_r(t)$ can be computed accurately.
3. If $\mathbf{n}_{0,u}$ is known accurately, $\mathbf{n}_u(t)$ can be reconstructed accurately using Eq. (4.11). However, if the initial numbers of moles of the unavailable species $\mathbf{n}_{0,u}$ are unknown, then asymptotic observers as described in Appendix E can be used to reconstruct the numbers of moles of the unavailable species under certain conditions. The asymptotic observers of Appendix E are similar to those proposed in Bastin and Dochain [11] and Srinivasan et al. [75]. The only difference regards the use of the extents of inlet flow and the discounting variable instead of the reaction invariants.

4.3 Open gas–liquid reaction systems

4.3.1 Minimal state representation

The linear transformations in Sections 3.2.1–3.2.2 for open G–L reaction systems lead to $(R + 2p_m + p_l + p_g + 2)$ variant states. In this section, it will be shown that the transformed model is minimal state representation, and conditions for minimality will be given. Before deriving the minimality conditions, it will be shown next that this transformed model satisfies the representation condition.

Representation condition

In the case of G–L reaction systems *without outlet*, the gas and liquid phases can be treated simultaneously. As a result, it was shown in Section 3.2.3 that the linear transformation leads to $(R + p_m + p_l + p_g)$ variant states. In contrast, when the two phases are treated separately, there are $2p_m$ extents of mass transfer. Since there are only p_m mass transfers between the gas and the liquid, the question arises as to whether it is possible to further reduce the number of extents of mass transfer from $2p_m$ to p_m when the liquid and gas phases are treated simultaneously. It will be shown next that such a reduction in the number of extents of mass transfer is not possible.

Theorem 4.3

Consider the subsystem of the transformed G–L reaction system given by Eqs. (3.21) and (3.27):

$$\begin{aligned}
 \dot{\mathbf{x}}_{m,l} &= \zeta - \frac{u_{out,l}}{m_l} \mathbf{x}_{m,l}, & \mathbf{x}_{m,l}(0) &= 0, \\
 \dot{\lambda}_l &= -\frac{u_{out,l}}{m_l} \lambda_l, & \lambda_l(0) &= 1, \\
 \dot{\mathbf{x}}_{m,g} &= \zeta - \frac{u_{out,g}}{m_g} \mathbf{x}_{m,g}, & \mathbf{x}_{m,g}(0) &= 0, \\
 \dot{\lambda}_g &= -\frac{u_{out,g}}{m_g} \lambda_g, & \lambda_g(0) &= 1.
 \end{aligned} \tag{4.12}$$

If the system (4.12) is locally state accessible, there does not exist a transformation Ψ that reduces the states of system (4.12). (See Proof in Appendix A.7)

Remark 4.1

Theorem 4.3 gives the condition under which further reduction of the transformed models Eqs. (3.21) and (3.25) is not possible. However, if $\frac{u_{out,g}}{m_g} = \frac{u_{out,l}}{m_l}$, $\mathbf{x}_{m,l}(t) = \mathbf{x}_{m,g}(t)$ and $\lambda_l(t) = \lambda_g(t)$ from Eq. (4.12). Hence, the number of states in system (4.12) reduces from $(2p_m+2)$ to (p_m+1) . These (p_m+1) states are $\mathbf{x}_{m,g}$ and λ_g in Eq. (4.12). However, this pathological case is rare in practice.

For the linear transformations given in Theorem 3.1 and Corollary 3.1, Ψ in Definition 4.1 is given by Eqs. (3.17), (3.25), (3.24) and (3.30). In addition, one can also define the inverse Ψ^{-1} so that the states \mathbf{n}_l and \mathbf{n}_g can be reconstructed from the transformed ones as described in Theorem 3.1 and Corollary 3.1. Hence, the representation condition of Definition 4.1 is fulfilled.

To simplify the representation of the transformed model, let us define the p_m -dimensional vector $\delta_m = \mathbf{x}_{m,g} - \mathbf{x}_{m,l}$ expressing the differences in the extents of mass transfer in the liquid and gas phases. The dynamic equations describing δ_m are:

$$\dot{\delta}_m = -\frac{u_{out,l}}{m_l} \delta_m + \left(\frac{u_{out,l}}{m_l} - \frac{u_{out,g}}{m_g} \right) \mathbf{x}_{m,g}, \quad \delta_m(0) = \mathbf{0}_{p_m}. \tag{4.13}$$

Moreover, δ_m can be used to represent $\mathbf{x}_{m,l}$. Then, the transformed state vectors ξ_1 and ξ_2 are: $\xi_1^T = [\mathbf{x}_r^T \mid \mathbf{x}_{m,g}^T \mid \delta_m^T \mid \mathbf{x}_{in,l}^T \mid \mathbf{x}_{in,g}^T \mid \lambda_l \mid \lambda_g]$ and $\xi_2^T = [\mathbf{x}_{iv,l}^T \mid \mathbf{x}_{iv,g}^T]$. Since the invariant states are constant, they can be dropped, and the linearly transformed models (3.21) and (3.25) can be written in the form of Eq. (4.3) with $\xi_{1,0} = [\mathbf{0}_R^T \mid \mathbf{0}_{p_m}^T \mid \mathbf{0}_{p_m}^T \mid \mathbf{0}_{p_l}^T \mid \mathbf{0}_{p_g}^T \mid 1 \mid 1]$ and

$$\tilde{\mathbf{f}} = \begin{bmatrix} \mathbf{f}_r(\boldsymbol{\xi}) \\ \boldsymbol{\zeta}(\boldsymbol{\xi}) \\ \mathbf{0}_{p_m} \\ \mathbf{0}_{p_l} \\ \mathbf{0}_{p_g} \\ 0 \\ 0 \end{bmatrix}, \quad \tilde{\mathbf{G}} = \begin{bmatrix} \mathbf{0}_{R \times p_l} & \mathbf{0}_{R \times p_g} & -\frac{\mathbf{x}_r}{m_l} & \mathbf{0}_{R \times 1} \\ \mathbf{0}_{p_m \times p_l} & \mathbf{0}_{p_m \times p_g} & \mathbf{0}_{p_m \times 1} & -\frac{\mathbf{x}_{m,g}}{m_g} \\ \mathbf{0}_{p_m \times p_l} & \mathbf{0}_{p_m \times p_g} & \frac{\mathbf{x}_{m,g} - \boldsymbol{\delta}_m}{m_l} & -\frac{\mathbf{x}_{m,g}}{m_l} \\ \mathbf{I}_{p_l} & \mathbf{0}_{p_l \times p_g} & -\frac{\mathbf{x}_{in,l}}{m_l} & \mathbf{0}_{p_l \times 1} \\ \mathbf{0}_{p_g \times p_l} & \mathbf{I}_{p_g} & \mathbf{0}_{p_g \times 1} & -\frac{\mathbf{x}_{in,g}}{m_g} \\ \mathbf{0}_{1 \times p_l} & \mathbf{0}_{1 \times p_g} & -\frac{\lambda_l}{m_l} & 0 \\ \mathbf{0}_{1 \times p_l} & \mathbf{0}_{1 \times p_g} & 0 & -\frac{\lambda_g}{m_g} \end{bmatrix}, \quad \mathbf{u} = \begin{bmatrix} \mathbf{u}_{in,l} \\ \mathbf{u}_{in,g} \\ \lambda_l \\ \lambda_g \end{bmatrix}, \quad (4.14)$$

where $\boldsymbol{\xi}_1$ is the $(R + 2p_m + v)$ -dimensional state vector with $v = p_l + p_g + 2$, $\tilde{\mathbf{f}}$ and $\tilde{\mathbf{G}} = [\tilde{\mathbf{g}}_1, \dots, \tilde{\mathbf{g}}_v]$ are the $(R + 2p_m + v)$ -dimensional vector fields, \mathbf{f}_r is the R -dimensional vector field, $\boldsymbol{\zeta}$ is the p_m -dimensional vector field, and \mathbf{u} is the v -dimensional input vector.

Minimality condition

The conditions under which Eqs. (4.3)–(4.14) is a minimal state representation of the G–L reaction system (3.9)–(3.10) are given in the following theorem.

Theorem 4.4 (Minimal state representation: G–L reactors with outlet)

Consider the G–L reaction system (3.9)–(3.10). If (i) $\text{rank}([\mathbf{N}^T \bar{\mathbf{W}}_{in,l} \mathbf{n}_{l0}]) = R + p_l + p_m + 1$ for the linear transformation of Theorem 3.1 for the liquid phase, and (ii) $\text{rank}([\bar{\mathbf{W}}_{in,g} \mathbf{n}_{g0}]) = p_g + p_m + 1$ for the linear transformation of Corollary 3.1 for the gas phase, and (iii) the system (4.3)–(4.14) is locally state accessible, then the transformed system Eqs. (4.3)–(4.14) is a minimal state representation of the system (3.9)–(3.10). (Proof follows from Lemma 4.2)

In G–L reaction systems, the accessibility distribution Δ has to be computed to check the minimal state representation. Hence, there is no straightforward condition such as $\text{rank}(\mathbf{J}(t))$ in homogeneous reaction systems to check the local state accessibility of the system (4.3)–(4.14).

When the reactions take place only in the liquid phase, as assumed in this thesis, the gas phase acts as an exchange layer between the gaseous inlets and the liquid phase on the one hand, and the volatile products from the liquid phase and the gaseous outlet on the other hand. Often, in such reaction systems, $\text{rank}([\bar{\mathbf{W}}_{in,g} \mathbf{n}_{g0}]) = \text{rank}([\bar{\mathbf{W}}_{in,g}]) = S_g < p_g + p_m$. Hence, Corollary 3.1 cannot be applied to transform the number of moles vector in the gas phase into extents and invariants. However, the numbers of moles in the liquid phase can be transformed, provided Conditions in Theorem 3.1 are satisfied. Then, the following corollary describes the conditions under which the systems (3.9) and (3.21) are minimal state representations.

Corollary 4.1

Consider the G–L reaction system (3.9)–(3.10). If (i) the number of species in the gas phase, $S_g < p_g + p_m$, (ii) $\text{rank}([\mathbf{N}^T \bar{\mathbf{W}}_{in,l} \mathbf{n}_{l0}]) = R + p_l + p_m + 1$ for the linear transformation of Theorem 3.1 for the liquid phase, and (iii) Eqs. (3.9) and (3.21) are locally state accessible, then Eqs. (3.9) and (3.21) are a minimal state representation of (3.9)–(3.10). (Proof follows from Lemma 4.2)

4.3.2 State reconstruction

Similar to homogeneous reaction systems, a flow-based approach for reconstructing the unavailable numbers of moles in the liquid phase using the minimal number of measurements will be developed for G–L reaction system next. This flow-based approach proceeds in two steps: (i) the computation of the extents of reaction, mass transfer, and flows from the available numbers of moles in the liquid and gas phases and the mass flowrates, and (ii) the reconstruction of the unavailable numbers of moles in the liquid and gas phases from the computed extents of reaction, mass transfer and flows, and the initial conditions of the unavailable species.

Let $\mathbf{n}_{l,a}(t)$ and $\mathbf{n}_{g,a}(t)$ be the $S_{l,a}$ and $S_{g,a}$ -dimensional vectors of the available numbers of moles in the liquid phase and the gas phase, respectively. In addition, the inlet and outlet flowrates in the liquid and gas phases ($\mathbf{u}_{in,l}$, $\mathbf{u}_{in,g}$, $u_{out,l}$, and $u_{out,g}$) are also measured. The stoichiometric matrix \mathbf{N} , the inlet matrices $\mathbf{W}_{in,l}$ and $\mathbf{W}_{in,g}$, the mass-transfer matrices $\mathbf{W}_{m,g}$ and $\mathbf{W}_{m,l}$ and the initial conditions \mathbf{n}_{l0} and \mathbf{n}_{g0} are known. The objective of this section is to reconstruct the unavailable numbers of moles in the liquid ($\mathbf{n}_{l,u}$) and the gas ($\mathbf{n}_{g,u}$), and to compute the extents of reaction in the liquid phase (\mathbf{x}_r), the extents of mass transfer ($\mathbf{x}_{m,g}$ and $\mathbf{x}_{m,l}$), the extents of inlet flow ($\mathbf{x}_{in,l}$ and $\mathbf{x}_{in,g}$), and the discounting variables (λ_l and λ_g) using as few measured numbers of moles as possible, and this without knowledge of the reaction-rate and mass-transfer-rate expressions.

Without loss of generality, it is assumed that the $S_{g,a}$ species available in the gas phase are involved in the mass transfers². The extents of mass transfer will be computed from information stemming from both phases, namely p_{m_g} extents will be computed from the gas phase, while $p_{m_l} = p_m - p_{m_g}$ extents will be computed from the liquid phase. In other words, the p_m transferring species are measured such that p_{m_g} species are measured in the gas phase and p_{m_l} are measured in the liquid phase. The extents of mass transfer and the mass-transfer matrices are noted accordingly. For instance, $\mathbf{x}_{m_g,g}$ and $\mathbf{x}_{m_g,l}$ represent the p_{m_g} -dimensional vectors of extents of mass transfer computed from gas-phase measurements for the gas phase and the liquid phase, respectively; $\mathbf{x}_{m_l,l}$ is the p_{m_l} -dimensional vector of extents of mass transfer computed from the liquid measurements and for the liquid phase; $\mathbf{W}_{m_g,g,a}$ is the $(S_{g,a} \times p_{m_g})$ mass-transfer matrix associated with the p_{m_g} mass transfers and the $S_{g,a}$ species; $\mathbf{W}_{m_l,l,a}$ is the $(S_{l,a} \times p_{m_l})$ mass-transfer matrix associated with the p_{m_l} mass transfers and the $S_{l,a}$ species; $\mathbf{W}_{m_g,l,a}$ is the $(S_{l,a} \times p_{m_g})$ mass-transfer matrix associated with the p_{m_g} mass transfers and the $S_{l,a}$ species.

With the $(S_{l,a} + S_{g,a})$ available numbers of moles, the measured flowrates, and the known information \mathbf{N} , $\mathbf{W}_{in,f}$, $\mathbf{W}_{m,f}$, and \mathbf{n}_{f0} , where $f = \{g, l\}$, the following differential-algebraic equations can be written for the liquid and gas phases:

- Algebraic equations obtained through the available numbers of moles $\mathbf{n}_{l,a}$ and total mass m_l in the liquid phase:

² The species not involved in mass transfer can be discarded without any information loss.

$$\mathbf{n}_{l,a} = \mathbf{N}_a^T \mathbf{x}_r + \mathbf{W}_{in,l,a} \mathbf{x}_{in,l} + \mathbf{W}_{m,l,a} \mathbf{x}_{m,l} + \mathbf{n}_{l0,a} \lambda_l, \quad (4.15)$$

$$m_l = \mathbf{1}^T \mathbf{x}_{m,l} + \mathbf{1}^T \mathbf{x}_{in,l} + \lambda_l m_{l0}. \quad (4.16)$$

- Differential equations for the unknown extents of inlet flow $\mathbf{x}_{in,l}$ and the unknown discounting variable λ_l in the liquid phase:

$$\dot{\mathbf{x}}_{in,l} = \mathbf{u}_{in,l} - \frac{u_{out,l}}{m_l} \mathbf{x}_{in,l}, \quad \mathbf{x}_{in,l}(0) = \mathbf{0}_{p_l}, \quad (4.17)$$

$$\dot{\lambda}_l = -\frac{u_{out,l}}{m_l} \lambda_l, \quad \lambda_l(0) = 1. \quad (4.18)$$

- Algebraic equations for the measured numbers of moles $\mathbf{n}_{g,a}$ and the unknown total mass m_g in the gas phase:

$$\mathbf{n}_{g,a} = \mathbf{W}_{in,g,a} \mathbf{x}_{in,g} - \mathbf{W}_{m,g,a} \mathbf{x}_{m,g} + \mathbf{n}_{g0,a} \lambda_g \quad (4.19)$$

$$m_g = \mathbf{1}^T \mathbf{x}_{m,g} + \mathbf{1}^T \mathbf{x}_{in,g} + \lambda_g m_{g0}. \quad (4.20)$$

- Differential equations for the unknown extents of inlet flow $\mathbf{x}_{in,g}$ and the unknown discounting variables λ_g in the gas phase:

$$\dot{\mathbf{x}}_{in,g} = \mathbf{u}_{in,g} - \frac{u_{out,g}}{m_g} \mathbf{x}_{in,g}, \quad \mathbf{x}_{in,g}(0) = \mathbf{0}_{p_g}, \quad (4.21)$$

$$\dot{\lambda}_g = -\frac{u_{out,g}}{m_g} \lambda_g, \quad \lambda_g(0) = 1.$$

- Differential equations for the unknown difference in mass-transfer extents δ_m in the gas and liquid phases:

$$\dot{\delta}_m(t) = -\frac{u_{out,l}(t)}{m_l(t)} \delta_m(t) + \left(\frac{u_{out,l}(t)}{m_l(t)} - \frac{u_{out,g}(t)}{m_g(t)} \right) \mathbf{x}_{m,g}(t), \quad \delta_m(0) = \mathbf{0}_{p_{m_g}}. \quad (4.22)$$

- Algebraic equations for the unknown extents of mass transfer in the liquid phase $\mathbf{x}_{m,g,l}$ computed using the gas measurements:

$$\mathbf{x}_{m,g,l}(t) = \mathbf{x}_{m,g}(t) - \delta_m(t). \quad (4.23)$$

The above differential-algebraic system consists of $(S_{l,a} + S_{g,a} + p_m + 2)$ algebraic equations and $(p_l + p_g + p_m + 2)$ differential equations. The number of unknown variables is $(R + p_g + p_l + 3p_m + 4)$. The following theorem specifies the minimal number of composition measurements needed to reconstruct the unknown variables.

Theorem 4.5 (Minimal number of measurement in G–L reaction systems)

Let the matrices \mathbf{N} , $\mathbf{W}_{m,g}$, $\mathbf{W}_{m,l}$, $\mathbf{W}_{in,l}$, $\mathbf{W}_{in,g}$, and the initial conditions \mathbf{n}_{l0} and \mathbf{n}_{g0} be known. Furthermore, let the quantities $\mathbf{n}_{g,a}(t)$, $\mathbf{n}_{l,a}(t)$, $\mathbf{u}_{in,l}(t)$, $\mathbf{u}_{in,g}(t)$, $u_{out,l}(t)$, and $u_{out,g}(t)$ be measured. If (i) $S_{l,a} + S_{g,a} \geq R + p_m$, (ii) $\text{rank}(\mathbf{W}_{m,g,g,a}) = p_{m_g}$, and (iii) $\text{rank}([\mathbf{N}_a^T, \mathbf{W}_{m_l,l,a}]) \geq R + p_{m_l}$, then the differential-algebraic equations in (4.15)–(4.23) can be solved to compute the $(R + p_g + p_l + 3p_m + 4)$ unknowns, namely, the extents

of reaction $\mathbf{x}_r(t)$, the extents of mass transfer in the liquid phase $\mathbf{x}_{m,l}(t)$, the extents of mass transfer in the gas phase $\mathbf{x}_{m,g}(t)$, the extents of liquid inlet $\mathbf{x}_{in,l}(t)$, the extents of gas inlet $\mathbf{x}_{in,g}(t)$, and the discounting variables in the liquid $\lambda_l(t)$ and the gas $\lambda_g(t)$, and the masses of the liquid $m_l(t)$ and the gas $m_g(t)$. (See proof in Appendix A.8)

If the initial conditions of the unavailable species in the liquid ($\mathbf{n}_{l0,u}$) and the gas ($\mathbf{n}_{g0,u}$) are available, the unavailable numbers of moles in the liquid ($\mathbf{n}_{l,u}(t)$) and the gas ($\mathbf{n}_{g,u}(t)$) can be computed from the computed $\mathbf{x}_r(t)$, $\mathbf{x}_{in,l}(t)$, $\mathbf{x}_{m,l}(t)$, $\mathbf{x}_{m,g}(t)$, $\mathbf{x}_{in,g}(t)$, $\lambda_l(t)$ and $\lambda_g(t)$ in Theorem 4.5 as follows:

$$\mathbf{n}_{l,u}(t) = \mathbf{N}_u^T \mathbf{x}_r(t) + \mathbf{W}_{in,l,u} \mathbf{x}_{in,l}(t) + \mathbf{W}_{m,l,u} \mathbf{x}_{m,l}(t) + \mathbf{n}_{l0,u} \lambda_l(t), \quad (4.24)$$

$$\mathbf{n}_{g,u}(t) = \mathbf{W}_{in,g,u} \mathbf{x}_{in,g}(t) - \mathbf{W}_{m,g,u} \mathbf{x}_{m,g}(t) + \mathbf{n}_{g0,u} \lambda_g(t). \quad (4.25)$$

Remarks.

- Conditions (i)-(iii) specify the minimal number of concentration measurements needed to compute the extents of reaction and mass transfer, i.e. $S_{l,a} + S_{g,a} = R + p_m$.
- In addition to at least $(R + p_m)$ concentration measurements, the p_l liquid inlet flowrates, the p_g gas inlet flowrates, the liquid outlet flowrate and the gas outlet flowrates need to be measured. Hence, the minimal number of measurements to compute all the extents and the discounting variables is $(R + p_m + p_g + p_l + 2)$. On the other hand, it follows from Theorem 4.4 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 $(R + p_m + p_l + p_g + 2)$ measurements, the p_m differential equations for the state δ_m are required to reconstruct the unavailable states.
- If the initial numbers of moles in the liquid phase $\mathbf{n}_{l0,u}$ are not known, then the asymptotic observers described in Appendix E can be used to estimate the unavailable concentrations in the liquid phase. Note that the computation of the various extents in the liquid and gas phases are independent of $\mathbf{n}_{l0,u}$.

4.4 Illustrative simulated examples

The concepts of minimal state representation and state reconstruction are illustrated next based on simulated homogeneous and G–L reaction systems. The ethanolysis of phthalyl chloride is considered as a homogeneous reaction system, while the chlorination of butanoic acid is considered as a G–L reaction systems.

4.4.1 Homogeneous reaction system

The startup of the CSTR reactor for the ethanolysis of phthalyl chloride described in Section 2.4.3 is considered to illustrate the concepts of minimal state representation and state reconstruction.

Minimal state representation

Let us define the vectors $\mathbf{x}_r = [x_{r,1}, x_{r,2}, x_{r,3}]^T$ and $\mathbf{x}_{in} = [x_{in,A}, x_{in,B}]^T$, where $x_{r,1}$, $x_{r,2}$ and $x_{r,3}$ are the reaction variants (or extents) for Reactions R1, R2 and R3, respectively, and $x_{in,A}$ and $x_{in,B}$ are the flow variants (or extents) corresponding to the inlets of species A and B . The vector $\mathbf{f}_r = \frac{m(\mathbf{x}_{in}, \lambda)}{\rho(\mathbf{x})} \mathbf{r}(\mathbf{x})$ and the derivatives $\frac{\partial \mathbf{f}_r}{\partial \mathbf{x}_r}$, $\frac{\partial \mathbf{f}_r}{\partial \mathbf{x}_{in}}$ and $\frac{\partial \mathbf{f}_r}{\partial \lambda}$ can be expressed as:

$$\begin{aligned} \rho^2 \frac{\partial \mathbf{f}_r}{\partial \mathbf{x}_r} &= m \rho \frac{\partial \mathbf{r}}{\partial \mathbf{x}_r} - m \mathbf{r} \frac{\partial \rho}{\partial \mathbf{x}_r}, \\ \rho^2 \frac{\partial \mathbf{f}_r}{\partial \mathbf{x}_{in}} &= [\mathbf{r} \mathbf{1}_p^T + m \frac{\partial \mathbf{r}}{\partial \mathbf{x}_{in}}] \rho - m \mathbf{r} \frac{\partial \rho}{\partial \mathbf{x}_{in}}, \\ \rho^2 \frac{\partial \mathbf{f}_r}{\partial \lambda} &= [\theta \mathbf{r} + m \frac{\partial \mathbf{r}}{\partial \lambda}] \rho - m \mathbf{r} \frac{\partial \rho}{\partial \lambda}, \end{aligned} \quad (4.26)$$

where $\theta = m_0 = 96.75$ kg for the linear transformation of Theorem 2.2.

The conditions of Theorem 4.1, $\text{rank}([\mathbf{N}^T \mathbf{W}_{in} \mathbf{n}_0]) = R + p + 1 = 6$, is fulfilled. Hence, the linear transformation of the numbers of moles does exist. Using the Symbolic Math toolbox of MATLAB[®] and Eq. (4.26), it was verified that $\text{rank}(\mathbf{J}(t)) = R = 3$. Since the two conditions of Theorem 4.1 are satisfied, Eq. (4.6) is a minimal state representation of order 6 for this reaction system.

State reconstruction

The reconstruction of unavailable numbers of moles from available ones and mass flowrates is demonstrated next. The numbers of moles are simulated and corrupted with additive zero-mean Gaussian noise. The standard deviation for each species is taken as 2 % of the maximum number of moles of that species, i.e. $\sigma_s = 0.02 n_s^{max}$ for $s = \{A, B, C, D, E, F, G\}$. The measurements of the numbers of moles of species A , B , and C ($S_a = 3$) are assumed to be available, every 1.25 h for 50 h, as shown in Figure 4.1. In addition, the time profiles of the measured flowrates are available, as shown in Figure 2.7c. The various matrices related to the available and the unavailable species are given as follows:

$$\begin{aligned}
\mathbf{N}_a &= \begin{bmatrix} -1 & -1 & 1 \\ 0 & -1 & -1 \\ 0 & -1 & 0 \end{bmatrix}; \quad \mathbf{W}_{in,a} = \begin{bmatrix} 0.0049 & 0 \\ 0 & 0.0217 \\ 0 & 0 \end{bmatrix}; \quad \mathbf{n}_{0,a} = \mathbf{0}_3; \\
\mathbf{N}_u &= \begin{bmatrix} 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ -1 & 0 & 1 & 1 \end{bmatrix}; \quad \mathbf{W}_{in,u} = \mathbf{0}_{4 \times 2}; \quad \mathbf{n}_{0,u} = \begin{bmatrix} 0 \\ 0 \\ 1.5 \\ 0 \end{bmatrix}.
\end{aligned} \tag{4.27}$$

The aim is to reconstruct the numbers of moles of the unavailable species using the available ones. Since $S_a = R = 3$ and $\text{rank}(\mathbf{N}_a) = R = 3$, Theorem 4.2 can be applied to reconstruct the unavailable numbers of moles. In Step (1), the extents of R1 ($x_{r,1}$), R2 ($x_{r,2}$) and R3 ($x_{r,3}$) are computed from the available measurements and shown in Figure 4.2. The reconstructed numbers of moles are shown in Figure 4.3. It can be seen that the reconstructed numbers of moles are comparable to the true ones for the species E , F , and G . However, the numbers of moles of the species D is poorly reconstructed.

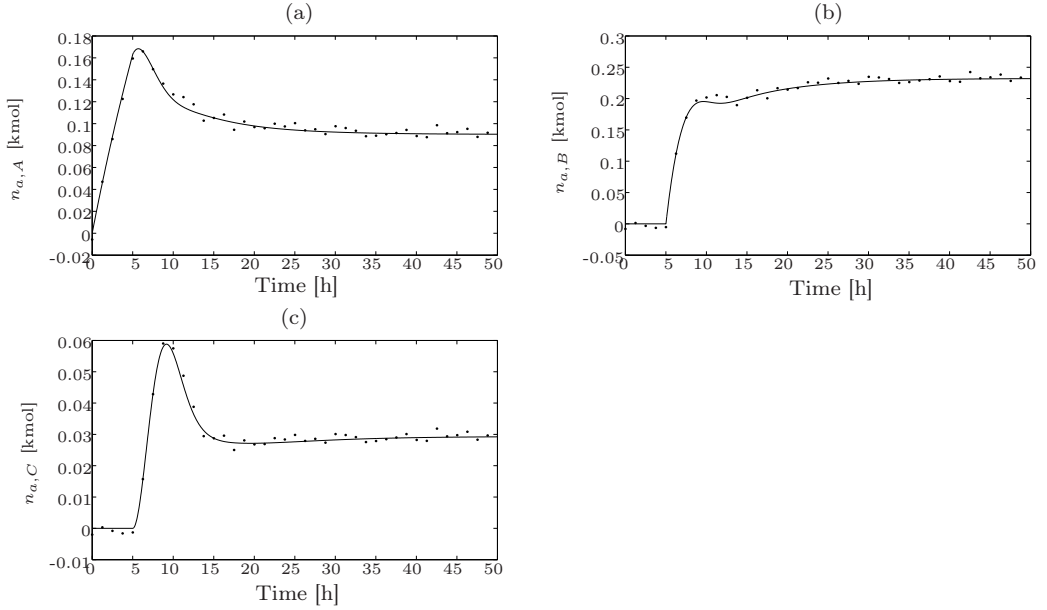


Figure 4.1 Ethanolysis of phthalyl chloride. Available numbers of moles: (a) number of moles of species A, (b) number of moles of species B), and (c) number of moles of species C. The solid lines indicate the simulated true numbers of moles and the markers indicate the measured (available) noisy numbers of moles.

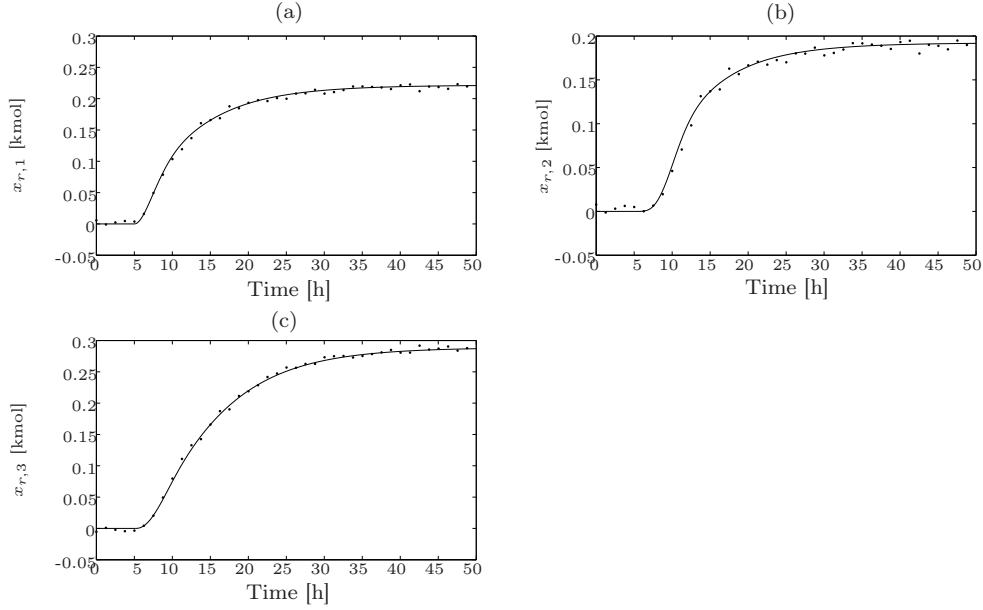


Figure 4.2 Ethanolysis of phthalyl chloride. Computed extents of reaction: (a) extent of R1, (b) extent of R2, and (c) extent of R3. The solid lines indicate the simulated true extents of reaction and the markers indicate the extents of reaction computed from the measurements.

4.4.2 Gas–liquid reaction system

The G–L reaction system for the chlorination of butanoic acid described in Section 3.3.2 is considered to illustrate the concept of state reconstruction. The noisy numbers of moles are simulated and corrupted with additive zero-mean Gaussian noise. The standard deviation for each species in the gas phase is taken as 0.003 kmol, i.e. $\sigma_s = 0.003$ kmol for $s = \{air, Cl_2, HCl\}$. Similarly, the standard deviation for each species in the liquid phase is taken as 0.02 kmol, i.e. $\sigma_s = 0.02$ kmol for $s = \{Cl_2, HCl, BA, MBA, DBA\}$.

The measurements of the numbers of moles of air, Cl_2 and HCl in the gas phase and of BA and MBA in the liquid phase are assumed to be available, every 54 sec for 1.5 h, as shown in Figures 4.4 and 4.5, respectively. In addition, the time profile of the measured inlet flowrate is available, as shown in Figure 3.6c, and a constant gas outlet of 511.2 kg h^{-1} is considered. The various matrices related to the available and the unavailable species are given as follows:

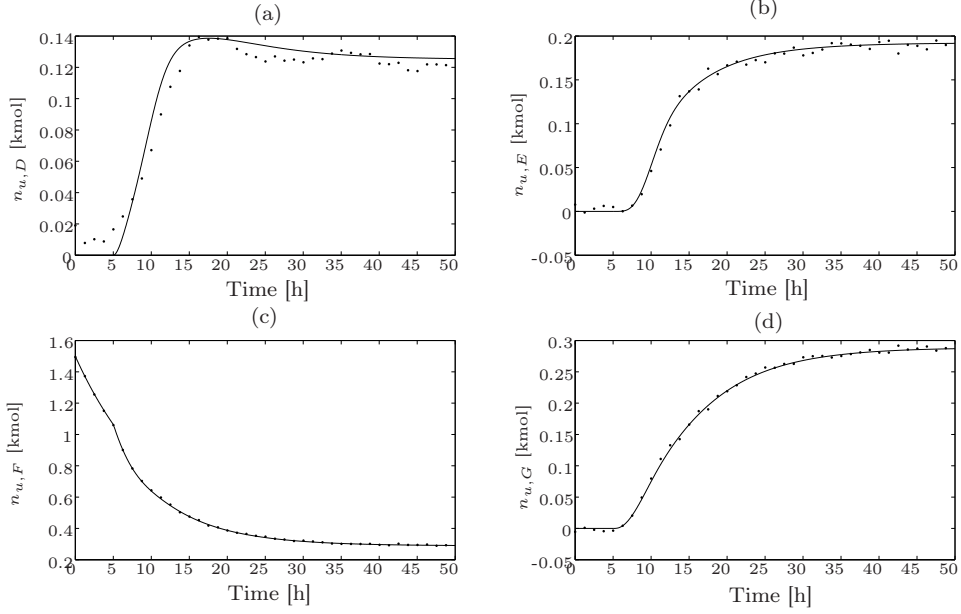


Figure 4.3 Ethanolysis of phthalyl chloride. Reconstructed numbers of moles: (a) numbers of moles of species D, (b) numbers of moles of species E, (c) numbers of moles of species F, and (d) numbers of moles of species G. The solid lines indicate the simulated true numbers of moles and the markers indicate the reconstructed numbers of moles.

$$\begin{aligned}
 \mathbf{W}_{in,g,a} &= \begin{bmatrix} 0 \\ 0.0141 \\ 0 \end{bmatrix}; & \mathbf{W}_{m_g,g,a} &= \begin{bmatrix} 0 & 0 \\ 0.0141 & 0 \\ 0 & 0.0274 \end{bmatrix}; & \mathbf{n}_{g0,a} &= \begin{bmatrix} 0.055 \\ 0 \\ 0 \end{bmatrix}; \\
 \mathbf{N}_a &= \begin{bmatrix} -1 & -1 \\ -1 & 0 \end{bmatrix}; & \mathbf{W}_{in,l,a} &= \mathbf{0}; & \mathbf{W}_{m_l,l,a} &= \mathbf{0}_{2 \times 2}; & \mathbf{n}_{l0,a} &= \begin{bmatrix} 13 \\ 0 \end{bmatrix}; \\
 \mathbf{N}_u &= \begin{bmatrix} -1 & 1 & 0 \\ -2 & 2 & 0 \end{bmatrix}; & \mathbf{W}_{m,l,u} &= \begin{bmatrix} 0.0141 & 0 \\ 0 & 0.0274 \\ 0 & 0 \end{bmatrix}; & \mathbf{W}_{in,l,u} &= \mathbf{0}; & \mathbf{n}_{l0,u} &= \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \quad (4.28)
 \end{aligned}$$

Note that there are no inlet and outlet streams associated with the liquid phase, i.e. $p_l = 0$.

The objective of this example is to reconstruct the numbers of moles in the liquid phase using the available measurements in the gas and liquid phases. The reaction system involves two mass transfers (Cl_2 and HCl , $p_m = 2$) and two reactions taking place in the liquid phase ($R = 2$). In the gas phase, $S_{g,a} = S_g = 3$ and $p_{m_g} = p_m = 2$. This leads to $p_{m_l} = 0$. Hence, the extent of Cl_2 mass transfer and the extent of HCl mass transfer can be computed from the gas measurements. In the liquid phase, $S_{l,a} = 2$. Since $S_{l,a} + S_{g,a} = 3 + 2 > R + p_m$, $\text{rank}(\mathbf{W}_{m_g,g,a}) = 2$, and $\text{rank}([\mathbf{N}_a^T, \mathbf{W}_{m_l,l,a}]) = 2 = R + p_{m_l}$, Theorem 4.5 can be applied to compute the various

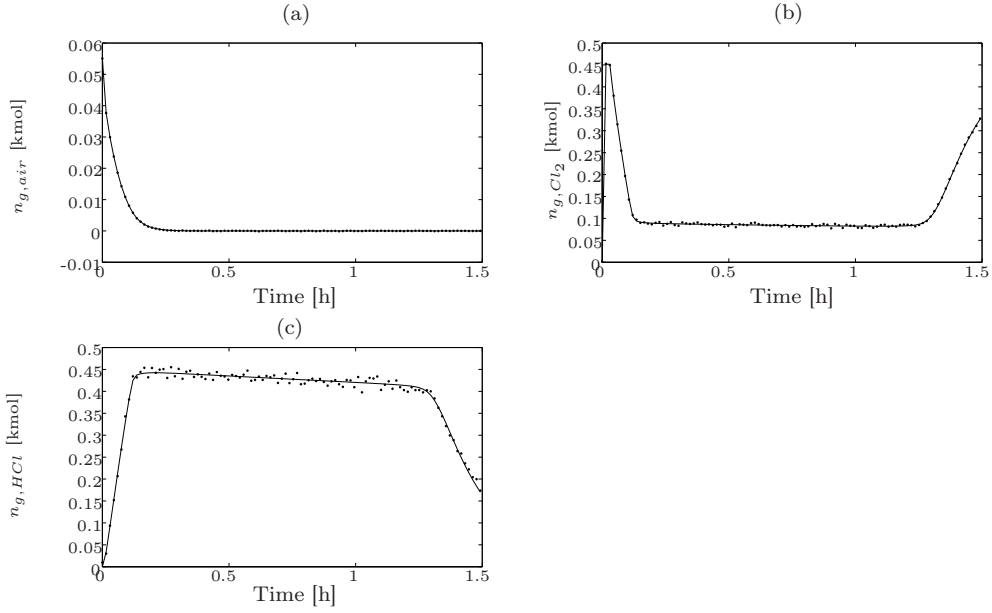


Figure 4.4 Chlorination of butanoic acid. Available numbers of moles in the gas phase: (a) numbers of moles of air, (b) numbers of moles of Cl_2 , and (c) numbers of moles of HCl . The solid lines indicate the simulated true numbers of moles and the markers indicate the noisy measured (available) numbers of moles.

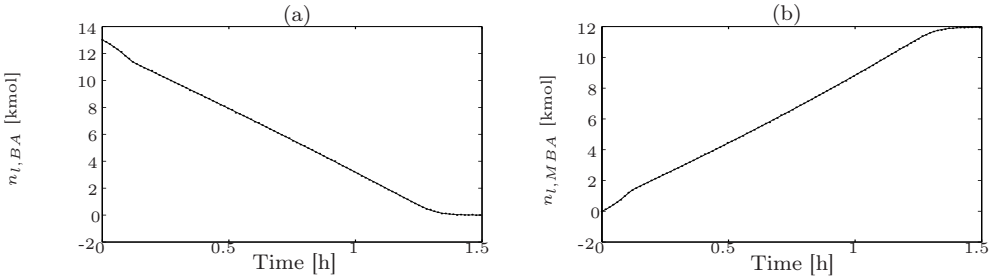


Figure 4.5 Chlorination of butanoic acid. Available numbers of moles in the liquid phase: (a) numbers of moles of BA ($n_{l,BA}$), and (b) numbers of moles of MBA ($n_{l,MBA}$). The solid lines indicate the simulated true numbers of moles and the markers indicate the measured (available) noisy numbers of moles.

extents and reconstruct the unavailable numbers of moles in the liquid phase. The differential-algebraic equations (4.15)–(4.23) for the chlorination of butanoic acid can be solved as follows.

- Since all the species in the gas phase are measured, m_g is computed using Eq. (3.13) from the available number of moles in the gas phase and shown in Figure 4.6a.
- Using the gas inlet and outlet flowrates and the computed gas mass, the extents of inlet x_{in,g,Cl_2} and the discounting variable $\lambda_g(t)$ are computed from Eq. (4.21). The extents of Cl_2 mass transfer x_{m_g,g,Cl_2} and HCl mass transfer $x_{m_g,g,\text{HCl}}$ in the gas phase

are computed from Eq. (4.19) using the measured numbers of moles in the gas phase and the computed x_{in,g,Cl_2} and $\lambda_g(t)$. The computed extents, x_{m,g,Cl_2} and $x_{m,g,HCl}$, are shown in Figures 4.6b–c.

- The extent of Cl_2 mass transfer (x_{m,g,l,Cl_2}) and the extent of HCl mass transfer ($x_{m,g,l,HCl}$) in the liquid phase can be computed from Eqs. (4.22)–(4.23) using the computed x_{m,g,Cl_2} and $x_{m,g,HCl}$. The computed δ_{m,Cl_2} and $\delta_{m,HCl}$ are shown in Figures 4.6d–e, while the computed x_{m,g,l,Cl_2} and $x_{m,g,l,HCl}$ are shown in Figure 4.7.
- Since $p_l = 0$ and $u_{out,l} = 0$, Eqs. (4.17) and (4.18) are dropped.
- Since $\text{rank}(\mathbf{N}_a) = R = 2$, the extent of R1 ($x_{r,1}$) and the extent of R2 ($x_{r,2}$) can be computed from Eq. (4.15) using the computed extents x_{m,g,l,Cl_2} and $x_{m,g,l,HCl}$, and the available numbers of moles in the liquid phase $\mathbf{n}_{l,a}$. The computed extents of R1 and R2 are shown in Figure 4.8.
- The computed extents in the liquid phase and information regarding the stoichiometric matrix, the mass-transfer matrix, and the initial conditions of the unavailable species can be used to reconstruct the numbers of moles of Cl_2 , HCl, and DBA in the liquid phase from Eq. (4.24). The reconstructed numbers of moles in the liquid phase are shown in Figure 4.9. Note that the numbers of moles of Cl_2 are poorly reconstructed for the time interval $[0.15, 1.2]$ h because of low signal-to-noise ratio.

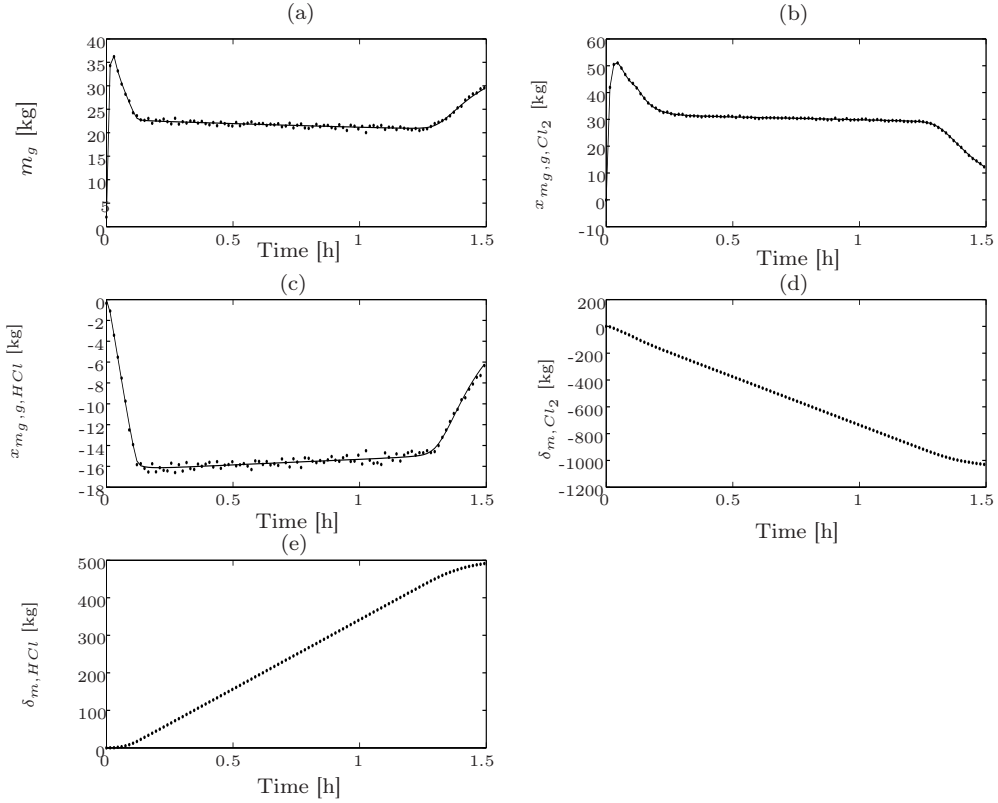


Figure 4.6 Chlorination of butanoic acid. Computed quantities using the measurements in the gas phase: (a) gas mass, (b) extent of mass transfer of Cl_2 in the gas phase, (c) extent of mass transfer of HCl in the gas phase, (d) difference variable associated with Cl_2 , and (e) difference variable associated with HCl . The solid lines indicate the simulated true quantities and the markers indicate the quantities in the gas phase computed using the measurements.

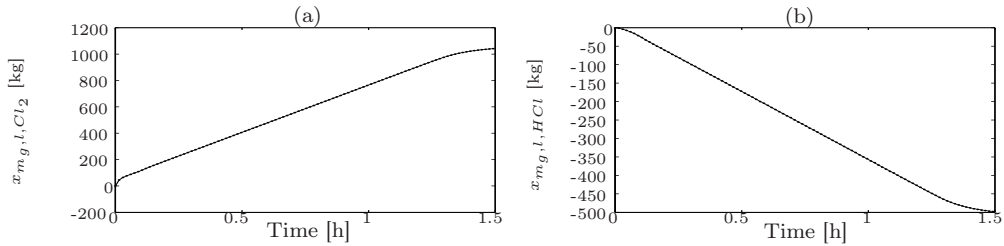


Figure 4.7 Chlorination of butanoic acid. Computed extents of mass transfer in the liquid phase: (a) extent of Cl_2 mass transfer in the liquid phase, and (b) extent of HCl mass transfer in the liquid phase. The solid lines indicate the simulated true extents of mass transfer and the markers indicate the extents of mass transfer in the liquid phase computed from the measurements.

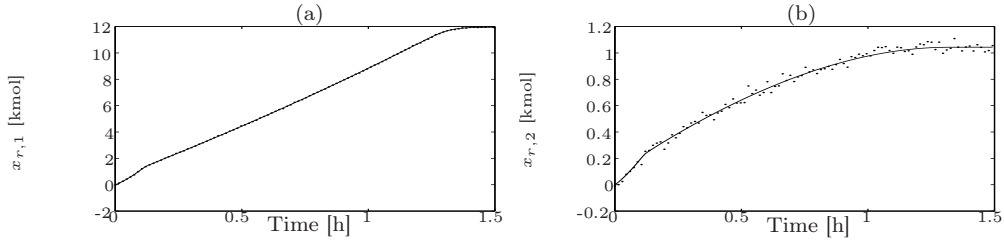


Figure 4.8 Chlorination of butanoic acid. Computed extents of reaction in the liquid phase: (a) extent of R1 in the liquid phase, and (b) extent of R2 in the liquid phase. The solid lines indicate the simulated true extents of reaction and the markers indicate the extents of reaction in the liquid phase computed from the measurements.

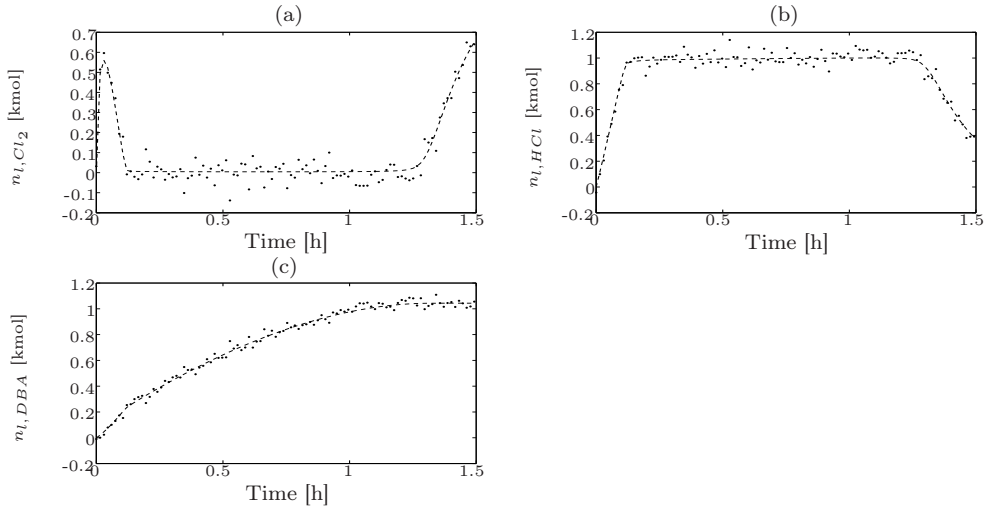


Figure 4.9 Chlorination of butanoic acid. Reconstructed numbers of moles in the liquid phase: (a) numbers of moles of Cl_2 , (b) numbers of moles of HCl , and (d) numbers of moles of DBA. The dashed lines indicate the simulated true numbers of moles and the markers indicate the reconstructed numbers of moles.

4.5 Summary

A minimal state representation is a dynamic model with no redundant states. The linear transformations in Chapters 2 and 3 decompose the numbers of moles into extents and invariant states. These invariants are constant since their dynamics have been removed. Hence, homogeneous reaction systems can be described by $(R+p+1)$ reaction and flow extents instead of the S original states, while G–L reaction systems can be described by $(R+2p_m+p_l+p_g+2)$ reaction, mass-transfer and flow extents instead of the (S_g+S_l) original states. Conditions have been derived under which the transformed models are indeed minimal state representations.

It has been shown that measured flowrates can be used to complement the transformations in order to reconstruct the unmeasured numbers of moles without knowledge

of reaction kinetics and mass-transfer rates. Furthermore, it has been shown that the minimal number of concentration measurements needed to reconstruct the unavailable species is R for homogeneous reactors and $(R + p_m)$ for G–L reactors.

The proposed flow-based approaches for reconstructing the unavailable concentrations can be useful for the identification of reaction and mass-transfer rates from measured data, as shown in the next chapter.

Chapter 5

Identification of reaction and mass-transfer rates from measured reaction data

The identification of a reliable kinetic model is important for building a first-principles model of a reaction system. In practice, this kinetic model is identified from measured reaction data obtained under a wide range of experimental conditions. The task of identification from measured data can be divided into two steps as follows:

1. Data transformation: Transform measured data in such a way that the extents of each reaction and each mass transfer can be computed. This way, each extent is independent of the contribution of the other reactions and mass transfers, and of operating conditions such as reactor type, initial conditions, inlet concentrations and flowrates.
2. Identification of reaction and mass-transfer rates: Determine the parameters of each reaction rate or each mass-transfer rate individually from the corresponding extent computed in the data-transformation step.

This chapter presents the identification of reaction and mass-transfer rates from concentrations and spectral data obtained in homogeneous and G–L reaction systems. For the analysis of concentrations from homogeneous and G–L reaction systems, two cases are considered: (a) the concentrations of all the species are measured, and (b) the concentrations of subsets of the species are measured (in the gas and liquid phases for G–L reaction systems). For Case (a), the linear transformations of Sections 2.3 and 3.2.1 are applied to compute the extents of reaction, mass transfer and flow directly from concentration data measured in homogeneous reactors or in the liquid phase of G–L reactors. For Case (b), the flow-based approaches of Sections 4.2.2 and 4.3.2 are applied, which use the measured flowrates and the concentrations of subsets of the species to compute the extents of reaction and mass transfer. Moreover, the means and variances of the computed extents are computed to study the error propagation in the data-transformation step for the case of concentration data corrupted with zero-mean Gaussian noise.

The analysis of spectral data from G–L reaction systems is also considered in this chapter. It is shown that the linear transformation in Section 3.2.1 can be explained to the case of measured spectral data, provided the pure-component spectra are known. Parameter estimation problems will be formulated to identify the parameters of each reaction rate or each mass-transfer rate, independently from the other rates, from the corresponding computed extents using the integral method. Furthermore, it is shown that

the incremental identification approach, which typically uses the differential method, can be adapted to the integral method using the computed individual extents.

It is not possible, without knowledge of the rate expressions, to compute the extents of reaction and mass transfer for the case of spectral data with unknown pure-component spectra. In such cases, the contributions of the reactions and mass transfers can be computed by removing the contributions of the inlet flows and the initial conditions. This leads to the so-called *reaction- and mass-transfer-variant (RMV) form* of spectral data. However, if the RMV-form of spectral data is rank deficient, the rank must be augmented before applying factor-analytical (FA) methods. In such cases, it is shown that gas consumption data can be used to augment the rank. Furthermore, it is shown that a parameter estimation problem can be formulated to identify simultaneously the parameters of the reaction and mass-transfer rates using the integral method.

Section 5.1 presents various approaches to compute the extents of reaction and mass transfer from concentrations in homogeneous and G–L reaction systems. In Section 5.2, the contributions of reactions and mass transfers are computed from spectral data. Section 5.3 formulates a parameter estimation problem that simultaneously identifies reaction- and mass-transfer-rate parameters based on the RMV-form of spectral data. In Section 5.4, estimation problems to identify the parameters of each reaction and each mass-transfer rates from the corresponding computed extents are formulated using the integral method. Section 5.5 illustrates two simulated examples for the identification of reaction and mass-transfer rates from noisy concentrations. Furthermore, rank augmentation of spectral data using gas consumption data is also illustrated for a G–L reaction system.

5.1 Computation of extents of reaction and mass transfer from concentrations

The linear transformations and the flow-based approaches developed in the previous chapters are applied next to compute the extents of reaction and mass transfer for homogeneous and G–L reaction systems.

5.1.1 Homogeneous reaction systems

Two cases will be distinguished depending upon the available measurements.

5.1.1.1 All concentrations measured

Let $\mathbf{c}(t_h)$ be the concentrations measured at the t_h time instant, with $h = 0, 1, \dots, H$. Let $V(t)$ denote the volume measured at time t ¹. Based on the linear transformation derived in Section 2.3, the following corollary states the conditions required to compute the extent of the i th reaction $x_{r,i}$, $\forall i = 1, \dots, R$ from $\mathbf{c}(t_h)$.

Corollary 5.1 (Linear transformation of $\mathbf{c}(t_h)$)

If (i) the matrices \mathbf{N} , \mathbf{W}_{in} and \mathbf{n}_0 are known, (ii) $\text{rank}([\mathbf{N}^T, \mathbf{W}_{in}, \mathbf{n}_0]) = R + p + 1$, and (iii) $\mathbf{c}(t_h)$ and $V(t_h)$ are measured, then the extent of the i th reaction $x_{r,i}$, $\forall i = 1, \dots, R$, at the t_h time instant can be computed as follows:

$$x_{r,i}(t_h) = (\mathbf{S}_0^T)_i V(t_h) \mathbf{c}(t_h), \quad (5.1)$$

where $(\mathbf{S}_0^T)_i$ denotes the i th row of the \mathbf{S}_0^T matrix and $V(t_h)$ is the volume measured at the t_h time instant. (Proof follows from Theorem 2.2)

The extents of the k th inlet at the t_h time instant ($x_{in,k}(t_h)$, $k = 1, \dots, p$) and the outlet extent ($x_{out}(t_h)$) can also be computed from $\mathbf{c}(t_h)$ and $V(t_h)$ as follows:

$$\begin{aligned} x_{in,k}(t_h) &= (\mathbf{M}_0^T)_k V(t_h) \mathbf{c}(t_h) \\ x_{out}(t_h) &= 1 - \mathbf{q}_0^T V(t_h) \mathbf{c}(t_h), \end{aligned} \quad (5.2)$$

where $(\mathbf{M}_0^T)_k$ denotes the k th row of the \mathbf{M}_0^T matrix. Furthermore, note that, even if the inlet and outlet flowrates are unknown, the linear transformation in Corollary 5.1 allows one to compute the individual extents of reaction and flow from the measured concentrations.

5.1.1.2 Subset of concentrations measured

Let $\mathbf{c}_a(t_h)$ be the concentrations of S_a available species at the t_h time instant. Based on the method proposed in Section 4.2.2, the following corollary states the conditions required to compute the extents of reaction $\mathbf{x}_r(t_h)$ from $\mathbf{c}_a(t_h)$.

Corollary 5.2 (Flow-based approach: Use of $\mathbf{c}_a(t_h)$)

If (i) the matrices \mathbf{N}_a and $\mathbf{W}_{in,a}$ are known, (ii) $\text{rank}(\mathbf{N}_a) = R$, and (iii) $\mathbf{c}_a(t_h)$, $\mathbf{u}_{in}(t)$, $u_{out}(t)$, and $V(t)$ are measured, then the extent of the i th reaction ($x_{r,i}$, $\forall i = 1, \dots, R$) at the t_h time instant can be computed in two steps as follows:

¹ In practice, concentrations are typically measured only infrequently, whereas the flowrates and the volume are available nearly continuously. This leads to low-resolution concentration data, denoted $\mathbf{c}(t_h)$, and high-resolution inlet and outlet flowrates and volume data, denoted $\mathbf{u}_{in}(t)$, $u_{out}(t)$ and $V(t)$, respectively.

1. Compute $\lambda(t)$, $\mathbf{x}_{in}(t)$, and $m(t)$:

$$\begin{aligned}\dot{\lambda}(t) &= -\frac{u_{out}(t)}{m(t)}\lambda(t), & \lambda(0) &= 1, \\ \dot{\mathbf{x}}_{in}(t) &= \mathbf{u}_{in}(t) - \frac{u_{out}(t)}{m(t)}\mathbf{x}_{in}(t), & \mathbf{x}_{in}(0) &= \mathbf{0}_p, \\ m(t) &= \mathbf{1}_p^T \mathbf{x}_{in}(t) + m_0\lambda(t).\end{aligned}\tag{5.3}$$

2. Compute the extent of the i th reaction, $x_{r,i}(t_h)$:

$$x_{r,i}(t_h) = (\mathbf{N}_a^{T+})_i (V(t_h)\mathbf{c}_a(t_h) - \mathbf{W}_{in,a}\mathbf{x}_{in}(t_h) - V_0\mathbf{c}_{0,a}\lambda(t_h)),\tag{5.4}$$

where $(\mathbf{N}_a^{T+})_i$ denotes the i th row of the (\mathbf{N}_a^{T+}) matrix. (Proof follows from Theorem 4.2)

The concentrations of the $S_u = S - S_a$ unmeasured species, $\mathbf{c}_u(t_h)$, can be reconstructed from the computed extents of reaction and flow and the initial conditions of the unavailable species as follows:

$$\mathbf{c}_u(t_h) = \frac{\mathbf{N}_u^T \mathbf{x}_r(t_h) + \mathbf{W}_{in,u}\mathbf{x}_{in}(t_h) + \mathbf{n}_{0,u}\lambda(t_h)}{V(t_h)}.\tag{5.5}$$

Remark 5.1

For situations where Condition (ii) in Corollary 5.1 does not hold, e.g. when $S < R + p + 1$, the extents of R reactions can be computed as described in Corollary 5.2.

Table 5.1 summarizes the computation of $x_{r,i}$ for special reactor configurations.

Table 5.1 Computation of the extents of reaction in various reactors from $\mathbf{c}_a(t_h)$

Reactor type	Computation of extent of i th reaction, $i = 1, \dots, R$
Batch	$x_{r,i}(t_h) = (\mathbf{N}_a^{T+})_i \left(V\mathbf{c}_a(t_h) - V_0\mathbf{c}_{0,a} \right)$
Semi-batch	$x_{r,i}(t_h) = (\mathbf{N}_a^{T+})_i \left(V(t_h)\mathbf{c}_a(t_h) - \mathbf{W}_{in,a}\mathbf{x}_{in}(t_h) - V_0\mathbf{c}_{0,a} \right)$
CSTR	$x_{r,i}(t_h) = (\mathbf{N}_a^{T+})_i \left(V_0\mathbf{c}_a(t_h) - \mathbf{W}_{in,a}\mathbf{x}_{in}(t_h) - V_0\mathbf{c}_{0,a}\lambda(t_h) \right)$

5.1.1.3 Error propagation in computed extents of reaction from noisy concentration measurements

In practice, concentration measurements are corrupted with noise. The error in concentration measurements may amplify during the computation of extents of reaction. Hence, it is important to study the error propagation during this step. Let $\mathbf{c}_c = \mathbf{c} + \mathbf{e}_c$

denote the noisy measurements, where \mathbf{e}_c is the S -dimensional vector of zero-mean Gaussian measurement noise with $\mathbf{e}_c \sim \mathcal{N}(\mathbf{0}_S, \mathbf{\Sigma}_c)$, and $\mathbf{\Sigma}_c$ is the $(S \times S)$ -dimensional noise variance matrix. It is assumed that noise-free flowrates and initial conditions are available. Then, the mean and variance of the extent of the i th reaction computed from all concentrations are as follows:

$$\begin{aligned} \mathbb{E}[x_{r,i}] &= (\mathbf{S}_0^T)_i V \mathbf{c} \\ \text{var}[x_{r,i}] &= V^2 (\mathbf{S}_0^T)_i \mathbf{\Sigma}_c (\mathbf{S}_0^T)_i^T, \end{aligned} \quad (5.6)$$

where $\mathbb{E}[\cdot]$ is the expectation operator and $\text{var}[\cdot]$ is the variance operator. Similarly, the mean and variance of the extent of the i th reaction computed using a subset of concentrations are as follows:

$$\begin{aligned} \mathbb{E}[x_{r,i}] &= (\mathbf{N}_a^{T+})_i (V \mathbf{c}_a - \mathbf{W}_{in,a} \mathbf{x}_{in} - \mathbf{n}_{0,a} \lambda) \\ \text{var}[x_{r,i}] &= V^2 (\mathbf{N}_a^{T+})_i \mathbf{\Sigma}_{c_a} (\mathbf{N}_a^{T+})_i^T. \end{aligned} \quad (5.7)$$

Eqs. (5.6) and (5.7) show that methods for the computation of the extents given in the previous sections give unbiased estimates of $x_{r,i}$. However, the variance of $x_{r,i}$ depends on the noise variances of all measured concentrations.

5.1.2 Gas–liquid reaction systems

The objective of this section is to compute the extents of reaction and mass transfer from concentration measurements. Note that the extents of mass transfer can be computed from either the gas or the liquid concentrations. However, the extents of reaction can only be computed from the liquid concentrations. Again, two cases can be distinguished depending upon the measurements available in the gas and liquid phases.

5.1.2.1 All liquid-phase concentrations measured

Let $\mathbf{c}_l(t_h)$ be the concentrations measured at the t_h time instant for the S_l species in the liquid phase. Based on Section 3.2, the following corollary states the conditions required to compute the extents of reaction $\mathbf{x}_r(t_h)$, and mass transfer $\mathbf{x}_{m,l}(t_h)$ from $\mathbf{c}_l(t_h)$.

Corollary 5.3 (Linear transformation of $\mathbf{c}_l(t_h)$)

If (i) the matrices \mathbf{N} , $\mathbf{W}_{m,l}$, $\mathbf{W}_{in,l}$, and \mathbf{c}_{l0} are known, (ii) $\text{rank}([\mathbf{N}^T \ \mathbf{W}_{m,l} \ \mathbf{W}_{in,l} \ \mathbf{n}_{l0}]) = R + p_l + p_m + 1$, and (iii) $\mathbf{c}_l(t_h)$ and $V_l(t_h)$ are measured, then the extent of the i th reaction $x_{r,i}(t_h)$ and the extent of the j th mass transfer in the liquid phase $x_{m,l,j}(t_h)$ can be computed using the following linear transformation:

$$\begin{bmatrix} x_{r,i}(t_h) \\ x_{m,l,j}(t_h) \end{bmatrix} = \begin{bmatrix} (\mathbf{S}_{l0}^T)_i \\ (\mathbf{M}_{m,l0}^T)_j \end{bmatrix} V_l(t_h) \mathbf{c}_l(t_h), \quad (5.8)$$

where $(\mathbf{S}_{l0}^T)_i$ denotes the i th row of the \mathbf{S}_{l0}^T matrix, and $(\mathbf{M}_{m,l0}^T)_j$ is the j th row of the $\mathbf{M}_{m,l0}^T$ matrix. (Proof follows from Theorem 3.1.)

Similarly, if the measurements of all the species in the gas phase $\mathbf{c}_g(t_h)$ are available, the linear transformation in Corollary 3.1 can be applied to compute the extent of the j th mass transfer $x_{m,g,j}(t_h)$ in the gas phase.

5.1.2.2 Subsets of concentrations measured in the gas and liquid phases

Let $\mathbf{c}_{g,a}(t_h)$ and $\mathbf{c}_{l,a}(t_h)$ be the $S_{g,a}$ - and $S_{l,a}$ -dimensional vectors of the measured concentrations in the gas and liquid phases at the t_h time instant, respectively. Based on Section 4.3.2, the following proposition states the conditions required to compute the extents of reaction and mass transfer from $\mathbf{c}_{g,a}(t_h)$ and $\mathbf{c}_{l,a}(t_h)$.

Proposition 5.1 (Flow-based approach: Use of $\mathbf{c}_{l,a}(t_h)$ and $\mathbf{c}_{g,a}(t_h)$)

Let the matrices \mathbf{N}_a , $\mathbf{W}_{m,g,g,a}$, $\mathbf{W}_{m,l,l,a}$, $\mathbf{W}_{m,g,l,a}$, $\mathbf{W}_{in,l,a}$, $\mathbf{W}_{in,g,a}$, the reactor volume V_t , and the initial conditions $\mathbf{n}_{l0,a}$ and $\mathbf{n}_{g0,a}$ be known. Furthermore, let the quantities $\mathbf{c}_{g,a}(t_h)$, $\mathbf{c}_{l,a}(t_h)$, $\mathbf{u}_{in,l}(t)$, $\mathbf{u}_{in,g}(t)$, $u_{out,l}(t)$, $u_{out,g}(t)$, $V_l(t)$, $m_l(t)$ and $m_g(t)$ be measured. If (i) $S_{l,a} + S_{g,a} \geq R + p_m$, (ii) $\text{rank}(\mathbf{N}_a) = R$, and (iii) $\text{rank}([\mathbf{N}_a^T, \mathbf{W}_{m,l,l,a}]) = R + p_{m_l}$, then the extents of reaction and mass transfer can be computed in three steps as follows:

1. Computation of the extents of mass transfer $\mathbf{x}_{m,g}$ in the gas phase:

$$\dot{\mathbf{x}}_{in,g}(t) = \mathbf{u}_{in,g}(t) - \frac{u_{out,g}(t)}{m_g(t)} \mathbf{x}_{in,g}(t), \quad \mathbf{x}_{in,g}(0) = \mathbf{0}_{p_g}, \quad (5.9a)$$

$$\dot{\lambda}_g(t) = -\frac{u_{out,g}(t)}{m_g(t)} \lambda_g, \quad \lambda_g(0) = 1, \quad (5.9b)$$

$$-\mathbf{W}_{m,g,g,a} \mathbf{x}_{m,g}(t_h) = \left(V_t - V_l(t_h) \right) \mathbf{c}_{g,a}(t_h) - \mathbf{W}_{in,g,a} \mathbf{x}_{in,g}(t_h) - \lambda_g(t_h) \mathbf{n}_{g0,a}. \quad (5.9c)$$

2. Computation of the extents of mass transfer $\mathbf{x}_{m,g,l}$ in the liquid phase:

$$\dot{\boldsymbol{\delta}}_m(t) = -\frac{u_{out,l}(t)}{m_l(t)} \boldsymbol{\delta}_m(t) + \left(\frac{u_{out,l}(t)}{m_l(t)} - \frac{u_{out,g}(t)}{m_g(t)} \right) \mathbf{x}_{m,g}(t), \quad \boldsymbol{\delta}_m(0) = \mathbf{0}_{p_{m_g}}, \quad (5.10a)$$

$$\mathbf{x}_{m,g,l}(t_h) = \mathbf{x}_{m,g}(t_h) - \boldsymbol{\delta}_m(t_h). \quad (5.10b)$$

3. Computation of the extents of reaction \mathbf{x}_r and mass transfer $\mathbf{x}_{m,l}$ in the liquid phase:

$$\dot{\mathbf{x}}_{in,l}(t) = \mathbf{u}_{in,l}(t) - \frac{u_{out,l}(t)}{m_l(t)} \mathbf{x}_{in,l}(t), \quad \mathbf{x}_{in,l}(0) = \mathbf{0}_{p_l}, \quad (5.11a)$$

$$\dot{\lambda}_l(t) = -\frac{u_{out,l}(t)}{m_l(t)} \lambda_l(t), \quad \lambda_l(0) = 1, \quad (5.11b)$$

$$\begin{aligned} \begin{bmatrix} \mathbf{N}_a^T & \mathbf{W}_{m_l,l,a} \end{bmatrix} \begin{bmatrix} \mathbf{x}_{m_l,l}(t_h) \\ \mathbf{x}_r(t_h) \end{bmatrix} &= V_l(t_h) \mathbf{c}_{l,a}(t_h) - \mathbf{W}_{in,l,a} \mathbf{x}_{in,l}(t) - \lambda_l(t) \mathbf{n}_{l0,a} \\ &\quad - \mathbf{W}_{m_g,l,a} \mathbf{x}_{m_g,l}(t_h). \end{aligned} \quad (5.11c)$$

(See Proof in Appendix A.9).

The differential-algebraic equations (5.9a)–(5.11c) can be solved as follows:

1. **Computation of the extents of mass transfer $\mathbf{x}_{m_g,g}$ in the gas phase:** In the first step, since the matrix $\mathbf{W}_{m_g,g,a}$ is full rank by construction, the differential-algebraic system (5.9a)–(5.9c) can be solved to compute the extents of mass transfer $\mathbf{x}_{m_g,g}$ involving the $S_{g,a}$ measured species in the gas phase.
2. **Computation of the extents of mass transfer $\mathbf{x}_{m_g,l}$ in the liquid phase:** In the second step, the extents of mass transfer $\mathbf{x}_{m_g,l}$ in the liquid phase corresponding to the $S_{g,a}$ species can be computed from Eqs. (5.10a)–(5.10b).
3. **Computation of the extents of reaction and mass transfer in the liquid phase:** In the third step, since the matrix $[\mathbf{N}_a^T, \mathbf{W}_{m_l,l,a}]$ is full rank by Assumption (iii) in Proposition 5.1, the remaining p_{m_l} extents of mass transfer $\mathbf{x}_{m_l,l}$ and the R extents of reaction \mathbf{x}_r can be computed by solving Eqs. (5.11a)–(5.11c).

Remarks.

1. If the volumetric flowrates ($q_{out,f}$, $\mathbf{q}_{in,f}$; $f \in \{g, l\}$) and the liquid volume V_l are measured, then $\frac{u_{out,f}}{m_f}$ can be computed from $\frac{q_{out,f}}{V_f}$, $f = \{g, l\}$ in Eqs. (5.9a)–(5.11c). Moreover, the masses of the liquid and gas phases need not be measured in this case.
2. The $S_{l,u}$ unavailable concentrations in the liquid phase $\mathbf{c}_{l,u}$ and the $S_{g,u}$ unavailable concentrations in the gas phase $\mathbf{c}_{g,u}$ can be reconstructed from the estimated extents as follows:

$$\mathbf{c}_{l,u}(t_h) = \frac{\mathbf{N}_u^T \mathbf{x}_r(t_h) + \mathbf{W}_{in,l,u} \mathbf{x}_{in,l}(t_h) + \mathbf{W}_{m,l,u} \mathbf{x}_{m,l}(t_h) + \mathbf{n}_{l0,u} \lambda_l(t_h)}{V_l(t_h)}, \quad (5.12)$$

$$\mathbf{c}_{g,u}(t_h) = \frac{\mathbf{W}_{in,g,u} \mathbf{x}_{in,g}(t_h) - \mathbf{W}_{m,g,u} \mathbf{x}_{m,g}(t_h) + \mathbf{n}_{g0,u} \lambda_g(t_h)}{V_t - V_l(t_h)}. \quad (5.13)$$

5.1.2.3 Special case: G–L reactors without outlet

The computation of extents of reaction and mass transfer for G–L reactors without outlet, such as batch and semi-batch reactors, is discussed next. As shown in Section 3.2.3, the gas and liquid phases can be treated simultaneously in such a case. When the con-

centrations of all species in the liquid phase are measured, Corollary 5.3 can be applied to compute the extents of reaction and mass transfer from the measurements.

The computation of the extents of reaction and mass transfer is described next when subsets of concentrations are measured in the gas and liquid phases.

Let $\bar{\mathbf{c}}_a(t_h) = \begin{bmatrix} \mathbf{c}_{g,a}(t_h) \\ \mathbf{c}_{l,a}(t_h) \end{bmatrix}$ be an \bar{S}_a -dimensional vector of measured concentrations in the gas and liquid phases at the t_h time instant, where $\bar{S}_a = S_{g,a} + S_{l,a}$. The $\bar{S}_a \times (p_g + p_l + p_m)$ -dimensional extended-inlet matrix of available species $\bar{\mathbf{W}}_{in,a}$ can be partitioned as: $\bar{\mathbf{W}}_{in,a} = \begin{bmatrix} \mathbf{W}_{in,g,a} & \mathbf{W}_{in,l,a} & \mathbf{W}_{m,a} \end{bmatrix}$, where $\mathbf{W}_{in,g,a}$ is the $(\bar{S}_a \times p_g)$ -dimensional matrix associated with the p_g gas inlet flowrates, $\mathbf{W}_{in,l,a}$ is the $(\bar{S}_a \times p_l)$ -dimensional matrix associated with the p_l liquid inlet flowrates, and $\mathbf{W}_{m,a}$ is the $(\bar{S}_a \times p_m)$ -dimensional matrix associated with the p_m mass transfers. Also, let $\bar{\mathbf{N}}_e := [\bar{\mathbf{N}}_a^T, \mathbf{W}_{m,a}]$ be the $\bar{S}_a \times (R + p_m)$ -dimensional extended stoichiometric matrix.

Corollary 5.4

If (i) the matrices $\bar{\mathbf{N}}_a$ and $\bar{\mathbf{W}}_{in,a}$ are known, (ii) $\text{rank}(\bar{\mathbf{N}}_e) = R + p_m$, and (iii) $\bar{\mathbf{c}}_a(t_h)$, $V_l(t)$, $\mathbf{u}_{in,g}(t)$, and $\mathbf{u}_{in,l}(t)$ are measured, then the extents of reaction ($x_{r,i}(t_h)$, $\forall i = 1, \dots, R$) and mass transfer ($x_{m,j}$, $\forall j = 1, \dots, p_m$) can be computed in two steps as follows:

1. Computation of $\mathbf{x}_{in,l}(t)$ and $\mathbf{x}_{in,g}(t)$:

$$\begin{aligned} \dot{\mathbf{x}}_{in,l}(t) &= \mathbf{u}_{in,l}(t), & \mathbf{x}_{in,l}(0) &= \mathbf{0}_{p_l}, \\ \dot{\mathbf{x}}_{in,g}(t) &= \mathbf{u}_{in,g}(t), & \mathbf{x}_{in,g}(0) &= \mathbf{0}_{p_g}. \end{aligned} \quad (5.14)$$

2. Computation of extents of the i th reaction and the j th mass transfer:

$$\begin{aligned} x_{r,i}(t_h) &= (\bar{\mathbf{N}}_e^+)_i (\bar{\mathbf{V}}_a(t_h) \bar{\mathbf{c}}_a(t_h) - \mathbf{W}_{in,g,a} \mathbf{x}_{in,g}(t_h) - \mathbf{W}_{in,l,a} \mathbf{x}_{in,l}(t_h) - \bar{\mathbf{V}}_a(0) \bar{\mathbf{c}}_a(0)), \\ x_{m,j}(t_h) &= (\bar{\mathbf{N}}_e^+)_{R+j} (\bar{\mathbf{V}}_a(t_h) \bar{\mathbf{c}}_a(t_h) - \mathbf{W}_{in,g,a} \mathbf{x}_{in,g}(t_h) - \mathbf{W}_{in,l,a} \mathbf{x}_{in,l}(t_h) - \bar{\mathbf{V}}_a(0) \bar{\mathbf{c}}_a(0)), \end{aligned} \quad (5.15)$$

where $(\bar{\mathbf{N}}_e^+)_i$ and $(\bar{\mathbf{N}}_e^+)_{R+j}$ are the i th row and the $(R+j)$ th rows of the matrix $(\bar{\mathbf{N}}_e^+)$, respectively, and $\bar{\mathbf{V}}_a = \text{diag}([(V_t - V_l)\mathbf{1}_{g,a}; V_l\mathbf{1}_{l,a}])$ is the $(\bar{S}_a \times \bar{S}_a)$ -dimensional matrix.

The $S_{l,u}$ unavailable concentrations in the liquid phase $\mathbf{c}_{l,u}$ and the $S_{g,u}$ unavailable concentrations in the gas phase $\mathbf{c}_{g,u}$ can be reconstructed from the estimated extents as follows:

$$\mathbf{c}_{l,u}(t_h) = \frac{\mathbf{N}_u^T \mathbf{x}_r(t_h) + \mathbf{W}_{in,l,u} \mathbf{x}_{in,l}(t_h) + \mathbf{W}_{m,u} \mathbf{x}_m(t_h) + \mathbf{n}_{l0,u}}{V_l(t_h)}, \quad (5.16)$$

$$\mathbf{c}_{g,u}(t_h) = \frac{\mathbf{W}_{in,g,u} \mathbf{x}_{in,g}(t_h) - \mathbf{W}_{m,u} \mathbf{x}_m(t_h) + \mathbf{n}_{g0,u}}{V_t - V_l(t_h)}. \quad (5.17)$$

5.1.2.4 Error propagation in computed extents of reaction and mass transfer from noisy concentration measurements

All liquid-phase concentrations measured

Let $\mathbf{c}_{l,c} = \mathbf{c}_l + \mathbf{e}_{l,c}$, denote the noisy concentration measurements in the liquid phase, where $\mathbf{e}_{l,c}$ is the S_l -dimensional vector of zero-mean Gaussian measurement noise with $\mathbf{e}_{l,c} \sim \mathcal{N}(\mathbf{0}_{S_l}, \mathbf{\Sigma}_{l,c})$, and $\mathbf{\Sigma}_{l,c}$ is the $(S_l \times S_l)$ -dimensional noise variance matrix. The mean and variance of the extents of the i th reaction and the j th mass transfer computed from the measured concentrations in the liquid phase are as follows:

- Means of $x_{r,i}$ and $x_{m,l,j}$:

$$\begin{aligned} \mathbb{E}[x_{r,i}] &= (\mathbf{S}_{l0}^T)_i V_l \mathbf{c}_l, \\ \mathbb{E}[x_{m,l,j}] &= (\mathbf{M}_{m,l0}^T)_j V_l \mathbf{c}_l. \end{aligned} \quad (5.18)$$

- Variances of $x_{r,i}$ and $x_{m,l,j}$:

$$\text{var}[x_{r,i}] = V_l^2 (\mathbf{S}_{l0}^T)_i \mathbf{\Sigma}_{l,c} (\mathbf{S}_{l0})_i, \quad (5.19)$$

$$\text{var}[x_{m,l,j}] = V_l^2 (\mathbf{M}_{m,l0}^T)_j \mathbf{\Sigma}_{l,c} (\mathbf{M}_{m,l0})_j. \quad (5.20)$$

Subsets of concentrations measured in the gas and liquid phases

In G-L reaction systems, since the extents of mass transfer can be computed from measurements in the liquid or/and gas phases, the measurement errors of one phase can propagate to the second phase. Let $\mathbf{c}_{f,c_a} = \mathbf{c}_{f_a} + \mathbf{e}_{f_a}$, with $f \in \{g, l\}$, denote the available concentrations in the f phase corrupted with noise, where \mathbf{e}_{f_a} is the S_{f_a} -dimensional vector of zero-mean Gaussian measurement noise with $\mathbf{e}_{f_a} \sim \mathcal{N}(\mathbf{0}_{S_{f_a}}, \mathbf{\Sigma}_{f_a})$, and $\mathbf{\Sigma}_{f_a}$ is the $(S_{f_a} \times S_{f_a})$ -dimensional diagonal noise variance matrix. The mean and variance of the extent of the j th mass transfer computed from measurements in the gas phase are as follows:

- Mean and variance of $x_{m_g,g,j}$:

$$\mathbb{E}[x_{m_g,g,j}] = -(\mathbf{W}_{m_g,g,a}^{-1})_j \left(V_g \mathbf{c}_{g,a} - \mathbf{W}_{in,g,a} \mathbf{x}_{in,g}(t_h) - \lambda_g(t_h) \mathbf{n}_{g0,a} \right), \quad (5.21)$$

$$\text{var}[x_{m_g,g,j}] = V_g^2 (\mathbf{W}_{m_g,g,a}^{-1})_j \mathbf{\Sigma}_{g,a} (\mathbf{W}_{m_g,g,a}^{-1})_j. \quad (5.22)$$

- Mean and variance of $x_{m_g,l,j}$:

$$\mathbb{E}[x_{m_g,l,j}] = x_{m_g,g,j} - \delta_{m,j}, \quad (5.23)$$

$$\text{var}[x_{m_g,l,j}] = \text{var}[x_{m_g,g,j}] + \text{var}[\delta_{m,j}] - 2 \text{cov}[x_{m_g,g,j}, \delta_{m,j}]. \quad (5.24)$$

The means of the extents of the i th reaction and j th mass transfer computed from measurements in the liquid and gas phases are as follows:

- Means of $x_{r,i}$ and $x_{m_l,l,j}$:

$$\mathbb{E}[x_{r,i}] = (\mathbf{N}_{l,a,e}^+)_i (V_l \mathbf{c}_{l,a} - \mathbf{W}_{in,l,a} \mathbf{x}_{in,l} - \lambda_l \mathbf{n}_{l0,a} - \mathbf{W}_{m_g,l,a} \mathbf{x}_{m_g,l}), \quad (5.25)$$

$$\mathbb{E}[x_{m_l,l,j}] = (\mathbf{N}_{l,a,e}^+)_{R+j} (V_l \mathbf{c}_{l,a} - \mathbf{W}_{in,l,a} \mathbf{x}_{in,l} - \lambda_l \mathbf{n}_{l0,a} - \mathbf{W}_{m_g,l,a} \mathbf{x}_{m_g,l}), \quad (5.26)$$

where $\mathbf{N}_{l,a,e} = [\mathbf{N}^T, \mathbf{W}_{m_l,l,a}]$ is the $S_{l,a} \times (R + p_{m_l})$ -dimensional extended stoichiometric matrix. The variances of $x_{r,i}$ and $x_{m_l,l,j}$ can also be computed.

As with homogeneous reaction systems, the computed extents of reaction and mass transfer are unbiased in G–L reaction systems. However, their variances are affected by the errors in the liquid- and gas-phase concentration measurements.

5.2 Computation of reaction and mass-transfer contributions from spectral data

Spectrometers, such as mid-infrared MIR, near-infrared NIR and ultraviolet/visible UV/VIS, measure indirectly the concentrations of many species on-line during the course of a reaction with short sampling times and without disturbing the reaction. Hence, huge amounts of information-rich spectral data are available at relatively low cost. The objective of this section is to compute the contributions of reaction and mass transfer from G–L reaction systems under certain conditions.

In addition to Assumptions (A1)–(A4) in Section 3.1.2, the following assumptions are considered: (A5) all reacting species absorb; (A6) the spectra depend linearly on the liquid concentrations, i.e. Beer’s law is valid; (A7) the corresponding S_l pure-component spectra are linearly independent and also independent of temperature and pressure; and (A8) the measured spectra are noise free.

Let $\mathbf{a}_l(t_h)$ denote the spectral (absorbance) vector for L channels at the t_h time instant measured in the liquid phase. With Assumptions (A5)–(A8), $\mathbf{a}_l(t_h)$ reads:

$$\mathbf{a}_l^T(t_h) = \mathbf{c}_l^T(t_h) \mathbf{E}, \quad (5.27)$$

where \mathbf{E} is the $(S_l \times L)$ -dimensional pure-component spectra matrix of the S_l absorbing and reacting species in the liquid phase. Upon multiplying both sides of Eq. (5.27) by $V_l(t_h)$, the L -dimensional volume-weighted spectral vector $\mathbf{a}_v(t_h)$ is defined as:

$$\mathbf{a}_v(t_h) := V_l(t_h) \mathbf{a}_l^T = V_l(t_h) \mathbf{c}_l^T(t_h) \mathbf{E} = \mathbf{n}_l^T(t_h) \mathbf{E}. \quad (5.28)$$

By substituting $\mathbf{n}_l(t)$ of Eq. (3.22) into Eq. (5.28), $\mathbf{a}_v(t_h)$ can be expressed in terms of the extents of reaction, mass transfer and flow, and the discounting factor as follows:

$$\begin{aligned} \mathbf{a}_v(t_h) &= (\mathbf{x}_r^T(t_h) \mathbf{N} + \mathbf{x}_{m,l}^T(t_h) \mathbf{W}_{m,l}^T + \mathbf{x}_{in,l}^T(t_h) \mathbf{W}_{in,l}^T + \lambda_l(t_h) \mathbf{n}_{l0}^T) \mathbf{E}, \\ &= \mathbf{x}_r^T(t_h) \mathbf{N} \mathbf{E} + \mathbf{x}_{m,l}^T(t_h) \mathbf{A}_m + \mathbf{x}_{in,l}^T(t_h) \mathbf{A}_{in} + \lambda_l(t_h) \mathbf{a}_0^T, \end{aligned} \quad (5.29)$$

where $\mathbf{A}_{in} := \mathbf{W}_{in,l}^T \mathbf{E}$ denotes the $(p_l \times L)$ -dimensional matrix of the liquid-inlet spectra, $\mathbf{A}_m := \mathbf{W}_m^T \mathbf{E}$ the $(p_m \times L)$ -dimensional matrix of the mass-transfer spectra, and $\mathbf{a}_0^T := \mathbf{n}_{l0}^T \mathbf{E}$ the L -dimensional vector of the initial spectrum.

For H observations, Eqs. (5.28) and (5.29) can be written in matrix form as:

$$\mathbf{A}_v = \mathbf{V}_l \mathbf{A} = \mathbf{V}_l \mathbf{C}_l \mathbf{E} = \mathcal{N}_l \mathbf{E}, \quad (5.30)$$

$$\mathbf{A}_v = \mathbf{X}_r \mathbf{N} \mathbf{E} + \mathbf{X}_{m,l} \mathbf{A}_m + \mathbf{X}_{in,l} \mathbf{A}_{in} + \mathbf{\Lambda}_l \mathbf{a}_0^T, \quad (5.31)$$

where \mathbf{A} and \mathbf{A}_v are the $(H \times L)$ -dimensional spectral and volume-weighted spectral matrices, $\mathbf{V}_l := \text{diag}(V_l(t_0), V_l(t_1), \dots, V_l(t_h))$ is the $(H \times H)$ -dimensional diagonal matrix of V_l , \mathbf{C}_l is the $(H \times S_l)$ -dimensional matrix of the liquid concentrations, \mathcal{N}_l is the $(H \times S_l)$ -dimensional matrix of numbers of moles in the liquid phase, \mathbf{X}_r is the $(H \times R)$ -dimensional matrix of the extents of reaction, $\mathbf{X}_{m,l}$ is the $(H \times p_m)$ -dimensional matrix of the extents of mass transfer, $\mathbf{X}_{in,l}$ is the $(H \times p_l)$ -dimensional matrix of the extents of flow, and $\mathbf{\Lambda}_l$ is the H -dimensional vector of the discounting variable. The h th rows of the matrices \mathbf{X}_r , $\mathbf{X}_{m,l}$, $\mathbf{X}_{in,l}$ and $\mathbf{\Lambda}_l$ are determined by integrating the differential equations (3.21) up to the t_h time instant. Note that the i th column of \mathbf{X}_r corresponds to the extents of the i th reaction for the H time instants, while the j th column of $\mathbf{X}_{m,l}$ corresponds to the extents of the j th mass transfer for the H time instants.

Eq. (5.30) is the factorization of the volume-weighted spectral matrix into the number of moles matrix and the pure-component spectra matrix. On the other hand, Eq. (5.31) separates the volume-weighted spectral matrix into four subspaces: (1) the R -dimensional reaction space spanned by the rows of $\mathbf{N} \mathbf{E}$; (2) the p_m -dimensional mass-transfer space spanned by the rows of \mathbf{A}_m ; (3) the p_l -dimensional liquid-inlet flow space spanned by the rows of \mathbf{A}_{in} ; and (4) the one-dimensional discounting variable space associated with the initial spectrum.

Depending on whether the pure-component spectra are known, two cases are considered: (a) known pure-component spectra, and (b) unknown pure-component spectra.

5.2.1 Known pure-component spectra: Computation of extents of reaction and mass transfer

If the pure-component spectra are known, the extents of reaction and mass transfer can be computed from the spectral data straightforwardly as stated by the next corollary.

Corollary 5.5

If (i) the matrices \mathbf{N} , $\mathbf{W}_{in,l}$, $\mathbf{W}_{m,l}$ and \mathbf{E} are known, (ii) the volume of the liquid phase is measured, and (iii) $\text{rank}([\mathbf{N}^T \ \mathbf{W}_{in,l} \ \mathbf{W}_{m,l} \ \mathbf{n}_{l0}]) = R + p_m + p_l + 1$, then the extents of reaction and mass transfer can be computed from the volume-weighted spectral data \mathbf{A}_v as follows:

$$\begin{bmatrix} \mathbf{X}_r^T \\ \mathbf{X}_{m,l}^T \end{bmatrix} = \begin{bmatrix} \mathbf{S}_{l0}^T \\ \mathbf{M}_{m,l0}^T \end{bmatrix} (\mathbf{E}^T)^+ \mathbf{A}_v^T. \quad (5.32)$$

(See Proof in Appendix A.10)

5.2.2 Unknown pure-component spectra: Transformation to spectral data in RMV-form

In many practical situations, the pure-component spectra are not known with sufficient accuracy and thus the transformation in Corollary 5.5 cannot be applied to spectral data. However, it is often possible to measure the initial spectrum \mathbf{a}_0 and the inlet spectra \mathbf{A}_{in} on-line without knowledge of the pure-component spectra. Then, it becomes possible to isolate the contributions of reaction and mass transfer from the spectral data along the line of Amrhein [2].

The extents of reaction and mass transfer in Eq. (5.31) are typically unknown, while the extents of flow and the discounting variables can be computed from the measured flowrates. Nevertheless, \mathbf{A}_v can be transformed to spectral data in reaction- and mass-transfer-variant form by removing the contributions of the inlet spectra \mathbf{A}_{in} and the initial spectrum \mathbf{a}_0 . This leads to the $(H \times L)$ spectral matrix in RMV-form, \mathbf{H}_{rm} :

$$\mathbf{H}_{rm} := \mathbf{A}_v - \mathbf{X}_{in,l}\mathbf{A}_{in} - \mathbf{\Lambda}_l\mathbf{a}_0^T = \mathbf{X}_r\mathbf{N}\mathbf{E} + \mathbf{X}_{m,l}\mathbf{A}_m. \quad (5.33)$$

Note that $\mathbf{H}_{rm} = \begin{bmatrix} \mathbf{X}_r & \mathbf{X}_{m,l} \end{bmatrix} \begin{bmatrix} \mathbf{N} \\ \mathbf{W}_{m,l}^T \end{bmatrix} \mathbf{E} = \mathbf{X}_{rm}\mathbf{N}_{rm}\mathbf{E}$, where \mathbf{X}_{rm} is the $H \times (R + p_m)$ -dimensional matrix of the extents of reaction and mass transfer, and \mathbf{N}_{rm} is the $(R + p_m) \times S_l$ -dimensional matrix. Note that $\mathbf{u}_{in}(t_h)$, $u_{out}(t_h)$, and $m_l(t_h)$, $\forall h = 0, 1, \dots, H$ need to be known for the computation of $\mathbf{X}_{in,l}$ and $\mathbf{\Lambda}_l$ in Eq. (5.33). The spectral matrix in RMV-form contains only the reaction-variant and mass-transfer-variant parts, which are typically unknown and are the subject of further investigation. Furthermore, if $\mathbf{X}_{in}\mathbf{A}_{in}$ is also unknown, then \mathbf{H}_{rm}^* can be defined as:

$$\mathbf{H}_{rm}^* := \mathbf{A}_v - \mathbf{\Lambda}_l\mathbf{a}_0^T = \mathbf{X}_{rm}\mathbf{N}_{rm}\mathbf{E} + \mathbf{X}_{in,l}\mathbf{A}_{in}. \quad (5.34)$$

5.2.3 Extensions to non-reacting and non-absorbing species

The computation of the contributions of reaction and mass transfer based on spectral data assumes that all species react and absorb. However, these assumptions rarely hold in practice. In this section, the assumptions will be relaxed, and the presence of non-reacting and non-absorbing species will be considered along the lines of Amrhein [2].

Non-absorbing reacting species

In practice, some reacting species do not absorb in the spectral regions of interest. For example, in G–L reaction systems, the species transferring from the gas phase to the liquid phase may not absorb. Let S_{ra} be the number of absorbing reacting species and S_{rn} the number of non-absorbing reacting species. Hence, the total number of species in the liquid phase $S_l = S_{ra} + S_{rn}$. Then, the pure-component spectra matrix can be redefined as: $\mathbf{E} := [\mathbf{0}_{S_{rn} \times L} \mid \mathbf{E}_{ra}]$, where the subscript $(\cdot)_{ra}$ and $(\cdot)_{rn}$ denote the quantities related to the S_{ra} and S_{rn} species, respectively. The matrices \mathbf{C}_l , \mathcal{N}_l , \mathbf{N} , $\mathbf{W}_{m,l}$, and $\mathbf{W}_{in,l}$ and \mathbf{n}_{l0} can be partitioned accordingly:

$$\mathbf{C}_l := [\mathbf{C}_{ra} \mid \mathbf{C}_{rn}], \quad \mathcal{N}_l := [\mathcal{N}_{ra} \mid \mathcal{N}_{rn}], \quad \mathbf{N} := [\mathbf{N}_{ra} \mid \mathbf{N}_{rn}], \quad (5.35)$$

$$\mathbf{W}_{m,l} = [\mathbf{W}_{m,ra} \mid \mathbf{W}_{m,rn}], \quad \mathbf{W}_{in,l} = \begin{bmatrix} \mathbf{W}_{in,ra} \\ \mathbf{W}_{in,rn} \end{bmatrix}, \quad \mathbf{n}_{l0} = \begin{bmatrix} \mathbf{n}_{l0,ra} \\ \mathbf{n}_{l0,rn} \end{bmatrix}. \quad (5.36)$$

With these matrices and \mathbf{E} , the volume-weighted spectral matrix \mathbf{A}_v in Eqs. (5.30) and (5.31) will be:

$$\mathbf{A}_v = \mathbf{V}_l \mathbf{C}_l \mathbf{E} = \mathbf{V}_l \mathbf{C}_{ra} \mathbf{E}_{ra} = \mathcal{N}_{ra} \mathbf{E}_{ra} \quad (5.37)$$

$$= (\mathbf{X}_r \mathbf{N}_{ra} \mathbf{E}_{ra} + \mathbf{X}_{m,l} \mathbf{A}_{m,ra} + \mathbf{X}_{in,l} \mathbf{A}_{in,ra} + \mathbf{\Lambda}_l \mathbf{a}_{0,ra}^T) \quad (5.38)$$

with

$$\mathbf{A}_{m,ra} = \mathbf{W}_{m,ra}^T \mathbf{E}_{ra}, \quad \mathbf{A}_{in,ra} = \mathbf{W}_{in,ra}^T \mathbf{E}_{ra}, \quad \mathbf{a}_{0,ra}^T = \mathbf{n}_{l0,ra}^T \mathbf{E}_{ra}. \quad (5.39)$$

Eq. (5.37) shows that a subset of concentrations can indirectly be measured by spectroscopy. For the case of spectral data with known pure-component spectra, the case of non-absorbing reacting species corresponds to the case of measuring a subset of concentrations. For the case of unknown pure-component spectra, the contributions of reaction and mass transfer can be computed as described in Section 5.2.2.

Non-reacting absorbing species

In practice, reactions are carried out in the presence of catalysts or in solvents. Solvents do not take part in the reactions and catalysts do not react. However, solvents and catalysts often absorb in the spectral regions of interest. Hence, they act as non-reacting absorbing species. Let S_{na} be the number of non-reacting but absorbing species and S_{ra} be the number of absorbing reacting species. Then, the number of absorbing species S_l can be redefined as $S_l := S_{ra} + S_{na}$. The $(S_l \times L)$ pure-component spectra matrix \mathbf{E} can be redefined as:

$$\mathbf{E} := \begin{bmatrix} \mathbf{E} \\ \mathbf{E}_{na} \end{bmatrix}, \quad (5.40)$$

where \mathbf{E}_{na} is an $(S_{na} \times L)$ -dimensional matrix of pure-component spectra of non-reacting species. The matrices \mathbf{N} , $\mathbf{W}_{in,l}$ and $\mathbf{W}_{m,l}$ are redefined as

$$\mathbf{N} := \left[\mathbf{N} \mid \mathbf{0}_{R \times S_{na}} \right], \mathbf{W}_{in,l} := \left[\frac{\mathbf{W}_{in,l}}{\mathbf{W}_{in,na}} \right], \quad (5.41)$$

$$\mathbf{W}_{m,l} := \left[\frac{\mathbf{W}_{m,l}}{\mathbf{W}_{m,na}} \right], \mathbf{n}_{l0} := \left[\frac{\mathbf{n}_{l0}}{\mathbf{n}_{l0,na}} \right]. \quad (5.42)$$

The subscript $(\cdot)_{na}$ denotes quantities related to the S_{na} species. The matrices \mathbf{X}_r , $\mathbf{X}_{in,l}$, $\mathbf{X}_{m,l}$ and $\mathbf{\Lambda}_l$ are defined as earlier.

If knowledge of the pure-component spectra of the non-reacting species and the reacting species are known, Corollary 5.5 can be applied to compute the extents of reaction, mass transfer and flows. If the pure-component spectra of the non-reacting species are unknown, then the extents of reaction and mass transfer can be computed from the spectral data as stated by the next corollary.

Corollary 5.6

Let us assume that all the transferring species are involved in the reactions. If (i) the matrices \mathbf{N} , $\mathbf{W}_{in,l}$ and $\mathbf{W}_{m,l}$ are known, (ii) the pure-component spectra of all reacting species are known, (iii) \mathbf{A}_{in} and \mathbf{a}_0 are measured, (iv) $\text{rank}([\mathbf{N}^T \ \mathbf{W}_{m,l}]) = R + p_m$, and (iv) $V_l(t)$, $\mathbf{u}_{in,l}(t)$, $u_{out,l}$ and $m_l(t)$ are measured, then the extents of reaction and mass transfer can be computed from the volume-weighted spectral data \mathbf{A} in two steps as follows:

Step 1: Computation of the spectral data in RMV-form \mathbf{H}_{rm} :

$$\mathbf{H}_{rm} := \mathbf{A}_v - \mathbf{X}_{in,l} \mathbf{A}_{in} - \mathbf{\Lambda}_l \mathbf{a}_0^T = \mathbf{X}_{rm} \mathbf{N}_{rm} \mathbf{E} = \mathbf{X}_{rm} \mathbf{E}_{rm}, \quad (5.43)$$

where $\mathbf{E}_{rm} = \mathbf{N}_{rm} \mathbf{E}$ is the $(R + p_m) \times L$ -dimensional matrix of reaction and mass-transfer spectra.

Step 2: Computation of the extents of reaction and mass transfer:

$$\mathbf{X}_{rm}^T = \begin{bmatrix} \mathbf{X}_r^T \\ \mathbf{X}_{m,l}^T \end{bmatrix} = (\mathbf{E}_{rm}^T)^+ \mathbf{H}_{rm}. \quad (5.44)$$

(See Proof in Appendix A.11)

As shown in Step 1 of Corollary 5.6, the non-reacting absorbing species do not affect the pre-treatment of spectral data to RMV-form.

5.2.4 Rank augmentation of spectral data using gas consumption data

Factor-analytical (FA) methods can be used for the calibration-free estimation of the extents of reaction and mass transfer from spectral data using prior knowledge about the extents and/or concentrations and the unknown pure-component spectra. However, if the spectral matrix is rank deficient, FA methods fail, and rank augmentation is required [3]. Next, rank deficiency of \mathbf{A} and \mathbf{H}_{rm} can be defined as follows:

Definition 5.1 (Rank deficiency of \mathbf{A} and \mathbf{H}_{rm})

\mathbf{A} and \mathbf{H}_{rm} are said to be rank deficient if $\text{rank}(\mathbf{A}) < S_l$ and $\text{rank}(\mathbf{H}_{rm}) < (R + p_a)$, respectively, where p_a is the number of absorbing transferring species. It follows that \mathbf{A} and \mathbf{H}_{rm} are said to be full rank if $\text{rank}(\mathbf{A}) = S_l$ and $\text{rank}(\mathbf{H}_{rm}) = (R + p_a)$, respectively.

If \mathbf{A} is rank deficient, the rank of \mathbf{A} must be augmented up to S_l . Alternatively, if \mathbf{H}_{rm} is of full rank $(R + p_a)$, FA methods can be applied to estimate the extents of reaction and mass transfer. However, if the RMV-form is rank deficient, the rank must be augmented to $(R + p_a)$. In this section, rank augmentation of spectral data in RMV-form using gas consumption data is discussed.

Computation of gas consumption data

Eq. (3.28) decomposes the S_g -dimensional vector of measured numbers of moles \mathbf{n}_g in the gas phase into the extents of mass transfer $\mathbf{x}_{m,g}$ and inlet flow $\mathbf{x}_{in,g}$, and the discounting variables λ_g . Since the mass flowrates in the gas phase are measured, $\mathbf{x}_{in,g}(t_h)$ and $\lambda_g(t_h)$ can be computed. Then, the p_m -dimensional vector of gas consumption, $\boldsymbol{\omega}_m(t_h)$, can be computed from Eq. (3.28):

$$\boldsymbol{\omega}_m(t_h) := -\check{\mathbf{W}}_{m,g} \mathbf{x}_{m,g}(t_h) = \check{\mathbf{n}}_g(t_h) - \check{\mathbf{W}}_{in,g} \mathbf{x}_{in,g}(t_h) - \check{\mathbf{n}}_{g0} \lambda_g(t_h), \quad (5.45)$$

where $\check{\mathbf{W}}_{m,g}$ is the $(p_m \times p_m)$ -dimensional mass-transfer matrix in the gas phase corresponding to the p_m transferring species, $\check{\mathbf{W}}_{in,g}$ the $(p_m \times p_g)$ -dimensional inlet-composition matrix, and $\check{\mathbf{n}}_g$ and $\check{\mathbf{n}}_{g0}$ the p_m -dimensional vectors of the measured and the initial numbers of moles corresponding to the p_m transferring species. For H observations, the $(H \times p_m)$ -dimensional matrix of gas consumption data, $\boldsymbol{\Omega}_m$, can be written as:

$$\boldsymbol{\Omega}_m := -\mathbf{X}_{m,g} \check{\mathbf{W}}_{m,g} = -\begin{bmatrix} \mathbf{X}_{m,gl} & \mathbf{X}_{m,lg} \end{bmatrix} \begin{bmatrix} \mathbf{W}_{m,gl} & \mathbf{0} \\ \mathbf{0} & \mathbf{W}_{m,lg} \end{bmatrix} \quad (5.46)$$

$$= -(\mathbf{X}_{m,gl} \mathbf{W}_{m,gl} + \mathbf{X}_{m,lg} \mathbf{W}_{m,lg}), \quad (5.47)$$

where $\mathbf{X}_{m,g}$ is the $(H \times p_m)$ -dimensional matrix of extent of mass transfer, $\mathbf{X}_{m,gl}$ and $\mathbf{X}_{m,lg}$ are the $(H \times p_{gl})$ and $(H \times p_{lg})$ matrices of extents of mass transfer of the p_{gl} and p_{lg} transferring species, and $\mathbf{W}_{m,gl}$ and $\mathbf{W}_{m,lg}$ are the $(p_m \times p_{gl})$ and $(p_m \times p_{lg})$ matrices of molecular weights corresponding to $\mathbf{X}_{m,gl}$ and $\mathbf{X}_{m,lg}$, respectively. The j th column of

$\mathbf{X}_{m,gl}$ corresponds to the extents of the j th mass transfer with $j = 1, \dots, p_{gl}$ for the H time instants, while the j th column of $\mathbf{X}_{m,lg}$ corresponds to the extents of the j th mass transfer with $j = p_{gl} + 1, \dots, p_m$ for the H time instants.

Rank augmentation of spectral data

Eqs. (5.31) and (5.33) are derived under the assumption that the gaseous species involved in mass transfer absorb. However, in many gas-liquid reaction systems, they may not absorb (for example H_2 and N_2 in UV spectroscopy). Hence, two cases are distinguished next.

Case 1: Gaseous species involved in mass transfer do not absorb

If the gaseous species involved in mass transfer do not absorb, \mathbf{H}_{rm} can be written as:

$$\mathbf{H}_{rm} = \mathbf{X}_r \mathbf{N} \mathbf{E}. \quad (5.48)$$

\mathbf{H}_{rm} contains the contribution of the unknown reaction rates but not that of the mass-transfer rates. Therefore, \mathbf{H}_{rm} is the spectral data in reaction-variant form, and thus its rank is typically R [2]. Hence, the rank-augmentation methods for homogeneous reaction systems can be applied to \mathbf{H}_{rm} [2].

Case 2: Gaseous species involved in mass transfer do absorb

If gaseous species involved in mass transfer absorb and $\text{rank}(\mathbf{H}_{rm}) = R + p_a$, then \mathbf{H}_{rm} is full rank. If only the species transferring from the gas to the liquid phase absorb, then $p_a = p_{gl}$. If all the species transferring between the liquid and gas phases absorb, $p_a = p_{gl} + p_{lg} = p_m$. If \mathbf{H}_{rm} is rank deficient, it is proposed to use gas consumption data for rank augmentation to $(R + p_a)$.

Let $\mathbf{\Omega}_a$ be the part of $\mathbf{\Omega}_m$ that corresponds to p_a , with $\mathbf{\Omega}_a := -\mathbf{X}_{m,r} \mathbf{W}_{m,r}^T$. If \mathbf{A}_{in} , \mathbf{a}_0 , $\mathbf{u}_{in,l}$, $\mathbf{u}_{out,l}$, \mathbf{m}_l , \mathbf{V}_l and $\mathbf{\Omega}_a$ are known or measured, the $H \times (L + p_a)$ augmented spectral matrix in the RMV-form can be computed as:

$$\mathbf{H}_{rm}^{aug} := [\mathbf{H}_{rm} \quad \mathbf{\Omega}_a] = \begin{bmatrix} \mathbf{X}_r & \mathbf{X}_{m,r} \end{bmatrix} \begin{bmatrix} \mathbf{N} & \mathbf{0} \\ \mathbf{W}_{m,r}^T & \mathbf{W}_{m,r}^T \end{bmatrix} \begin{bmatrix} \mathbf{E} & \mathbf{0}^T \\ \mathbf{0} & \mathbf{I}_{p_a} \end{bmatrix} = \mathbf{X}_{rm} \mathbf{N}_{rm}^{aug} \mathbf{E}^{aug}, \quad (5.49)$$

where \mathbf{N}_{rm}^{aug} is the $(R + p_a) \times (S_l + p_a)$ augmented stoichiometric matrix and \mathbf{E}^{aug} the $(S_l + p_a) \times (L + p_a)$ augmented pure-component spectral matrix.

Since $\text{rank}(\mathbf{X}_{rm}) = (R_l + p_a)$, $\text{rank}(\mathbf{E}^{aug}) = (S_l + p_a)$, and $\text{rank}(\mathbf{N}_{rm}^{aug}) = R + p_a$, then $\text{rank}(\mathbf{H}_{rm}^{aug}) = \min(R + p_a, S_l + p_a) = R + p_a$.

5.3 Simultaneous identification of rate parameters using the RMV-form of measured spectral data

This subsection discusses the simultaneous estimation of reaction and mass-transfer parameters from spectral data in RMV-form when the reaction- and mass-transfer-rate expressions are known and the pure-component spectra are possibly unknown. For such a scenario, various so-called hard-modeling methods have been proposed, which solve a constrained nonlinear regression problem [2, 80]. If the liquid volume, the inlet and outlet flowrates, and the masses in the liquid and the gas phases are measured, then a constrained nonlinear regression problem can be solved to estimate the parameters of the given reaction- and mass-transfer rates from the RMV-form of measured spectral data as follows:

$$\begin{aligned}
\min_{\boldsymbol{\theta}} J_{rm}, \quad J_{rm} &:= \left\| [\mathbf{I}_H - \mathbf{X}_{rm}(\boldsymbol{\theta}) \mathbf{X}_{rm}^+(\boldsymbol{\theta})] \mathbf{H}_{rm} \right\| \\
\text{s.t. } \dot{\mathbf{x}}_r(\boldsymbol{\theta}, t_h) &= V_l \mathbf{r}(\mathbf{c}_l, \boldsymbol{\theta}) - \frac{u_{out,l}}{m_l} \mathbf{x}_r(\boldsymbol{\theta}, t_h), & \mathbf{x}_r(\boldsymbol{\theta}, 0) &= \mathbf{0}_R, \\
\dot{\mathbf{x}}_{m,l}(\boldsymbol{\theta}, t_h) &= \boldsymbol{\zeta}(\mathbf{c}_l, \mathbf{c}_g, \boldsymbol{\theta}) - \frac{u_{out,l}}{m_l} \mathbf{x}_{m,l}(\boldsymbol{\theta}, t_h), & \mathbf{x}_{m,l}(\boldsymbol{\theta}, 0) &= \mathbf{0}_{p_m}, \\
\dot{\mathbf{x}}_{in,l}(t_h) &= \mathbf{u}_{in,l} - \frac{u_{out,l}}{m_l} \mathbf{x}_{in,l}(t_h), & \mathbf{x}_{in,l}(0) &= \mathbf{0}_{p_l}, \\
\dot{\lambda}_l(t_h) &= -\frac{u_{out,l}}{m_l} \lambda_l(t_h), & \lambda_l(0) &= 1, \\
\dot{\mathbf{x}}_{in,g}(t_h) &= \mathbf{u}_{in,g} - \frac{u_{out,g}}{m_g} \mathbf{x}_{in,g}(t_h), & \mathbf{x}_{in,g}(0) &= \mathbf{0}_{p_l}, \\
\dot{\lambda}_g(t_h) &= -\frac{u_{out,g}}{m_g} \lambda_g(t_h), & \lambda_g(0) &= 1, \\
\dot{\boldsymbol{\delta}}_m(t_h) &= -\frac{u_{out,g}}{m_g} \boldsymbol{\delta}_m(t_h) + \left(\frac{u_{out,l}}{m_l} - \frac{u_{out,g}}{m_g} \right) \mathbf{x}_{m,l}(\boldsymbol{\theta}, t_h), & \boldsymbol{\delta}_m(0) &= \mathbf{0}, \\
\mathbf{x}_{m,g}(t_h) &= \mathbf{x}_{m,l}(\boldsymbol{\theta}, t_h) + \boldsymbol{\delta}_m(t_h), \\
\mathbf{c}_l(\boldsymbol{\theta}, t_h) &= \frac{(\mathbf{N}^T \mathbf{x}_r(t_h) + \mathbf{W}_{in,l} \mathbf{x}_{in,l}(t_h) + \mathbf{W}_{m,l} \mathbf{x}_{m,l}(t_h) + \mathbf{n}_{l0} \lambda_l(t_h))}{V_l(t_h)}, \\
\mathbf{c}_g(\boldsymbol{\theta}, t_h) &= \frac{(\mathbf{W}_{in,g} \mathbf{x}_{in,g}(t_h) - \mathbf{W}_{m,g} \mathbf{x}_{m,g}(t_h) + \mathbf{n}_{g0} \lambda_g(t_h))}{V_t - V_l(t_h)}, \\
\boldsymbol{\theta}^L &\leq \boldsymbol{\theta} \leq \boldsymbol{\theta}^U,
\end{aligned} \tag{5.50}$$

where J_{rm} is the cost to minimize by adjusting the unknown l -dimensional vector of reaction- and mass-transfer-rate parameters $\boldsymbol{\theta}$, $\|\cdot\|$ a matrix norm, $\mathbf{X}_{rm}(\boldsymbol{\theta})$ the $(H \times L)$ -dimensional matrix of the extents of reaction and mass transfer simulated using the dynamic model, $\mathbf{c}_l(\boldsymbol{\theta}, t_h)$ the S_l -dimensional vector of the simulated concentrations in the liquid phase at the t_h time instant, and $\mathbf{c}_g(\boldsymbol{\theta}, t_h)$ the S_g -dimensional vector of the simulated concentrations in the gas phase.

J_{rm} minimizes the projection errors of \mathbf{H}_{rm} on the space spanned by the columns of $\mathbf{X}_{rm}(\boldsymbol{\theta})$ by adjusting the parameter vector $\boldsymbol{\theta}$. The estimation problem seeks the optimal

vector θ^* with the corresponding optimal estimate of the extents of reaction and mass transfer $\mathbf{X}_{rm}(\theta^*)$. Additional constraints such as ranges of pure-component spectra, and unimodality on rates can be added to the estimation problem.

In Eq. (5.50), $\mathbf{c}_g(\theta, t_h)$ is simulated by integrating the dynamic model. However, if the concentrations in the gas phase $\mathbf{c}_g(t_h)$ are available, then $\mathbf{c}_g(t_h)$ can be used to simulate the differential equation of $\mathbf{x}_{m,l}$ of Eq. (5.50), and the differential equations for λ_g , $\mathbf{x}_{in,g}$ and δ_m can be removed from Eq. (5.50).

5.4 Individual identification of reaction and mass-transfer rates using the integral method

In Section 5.1, measured data were transformed to compute the extents of reaction and mass transfer. The next step is to identify the parameters of the reaction and mass-transfer rates.

One approach consists in calculating the reaction and mass-transfer rates through differentiation of the computed extents from concentration data. Parameter estimation for the individual reactions and mass transfers can be performed by fitting the given reaction kinetic or mass-transfer model to the computed rates [16]. This approach corresponds to the so-called *differential method* of kinetic identification.

Alternatively, the unknown rate parameters can be estimated by comparing the model predictions obtained by integrating the given rate expressions and the measured concentrations. This approach corresponds to the *integral method* of kinetic identification. Note that the parameter estimates obtained using the integral method are statistically optimal in the maximum likelihood sense in the absence of structural uncertainty and for Gaussian measurement noise [10]. The integral method can also be used in conjunction with computed extents instead of measured concentrations.

This section will first discuss the concept of incremental identification of a rate model using the integral method. Then, the estimation of rate parameters using computed extents will be formulated. Finally, various incremental identification approaches will be proposed and compared.

5.4.1 Incremental identification of a rate model using the integral method

In the literature, the incremental identification approach is closely related to the *differential method* of kinetic identification, whereby the reaction and mass-transfer rates are obtained by differentiation of concentration data, as shown in Figure 1.3 [56, 17].

In Section 5.1, various transformations have been developed to compute the extents of reaction and mass transfer from measurements without knowledge of the reaction and mass-transfer rates. This fact can be exploited to investigate kinetic models using the *integral method* and the computed individual extents. The incremental identification

approach of Figure 1.3 that uses the differential method can be adapted to the integral method as shown in Figure 5.1. The contributions of reaction and mass transfer to each species are computed using concentration, volume and flowrate measurements and balance equations. If the reaction stoichiometry is unknown, candidate reactions can be tested using target factor analysis as described in [4, 15]. The extents of the individual reactions and mass transfers can be computed from the concentrations, volume and flowrate measurements using information regarding the stoichiometric, the inlet compositions, knowledge of the species transferring between phases, and the initial conditions as described in Section 5.1. The computed extents can then be used to discriminate a set of model candidates and estimate parameters as described in the next section.

Since the transformations to compute the extents of reaction and mass transfer in Section 5.1.1 do not introduce bias in the computed extents, the parameter refinement step of [17] to eliminate bias in the rate parameters is not required. Hence, the identified kinetic model can directly be validated using appropriate validation methods, as shown in Figure 5.1. If the validated model is acceptable, the identification process terminates. If the validated model is not acceptable, new experiments have to be performed. New experiments are commonly designed for two cases: (i) identification of model structure (model discrimination), and (ii) parameter estimation [7, 44].

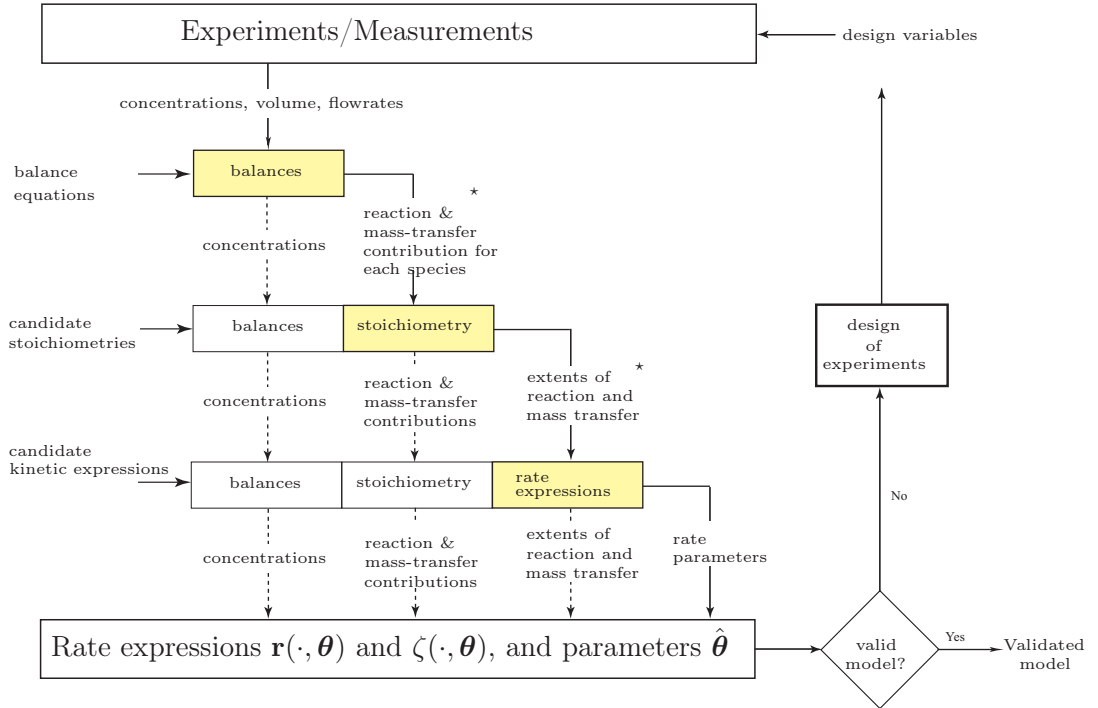


Figure 5.1 Incremental identification of a rate model using the integral (extent-based) method (*: the reaction and mass-transfer contributions are expressed in terms of concentrations, and not rates).

5.4.2 Rate parameter estimation using the computed extents of reaction and mass transfer

For the i th reaction, let $\hat{\mathbf{x}}_{r,i}$ and $\mathbf{x}_{r,i}$ denote the H -dimensional vectors of computed (according to the linear transformations of Section 5.1) and simulated (according to a postulated rate law involving the parameters $\boldsymbol{\theta}_{r,i}$) extents of reaction at H time instants. The following parameter estimation problem can be formulated:

$$\begin{aligned} \min_{\boldsymbol{\theta}_{r,i}} J_i &= (\hat{\mathbf{x}}_{r,i} - \mathbf{x}_{r,i}(\boldsymbol{\theta}_{r,i}))^T \mathbf{W}_r (\hat{\mathbf{x}}_{r,i} - \mathbf{x}_{r,i}(\boldsymbol{\theta}_{r,i})) \\ \text{s.t.} \quad \dot{x}_{r,i}(t_h, \boldsymbol{\theta}_{r,i}) &= r_i(\mathbf{c}_l(t_h), \boldsymbol{\theta}_{r,i}) V_l(t_h) - \frac{u_{out,l}(t_h)}{m_l(t_h)} x_{r,i}(t_h), \quad x_{r,i}(0) = 0, \\ \boldsymbol{\theta}_{r,i}^L &\leq \boldsymbol{\theta}_{r,i} \leq \boldsymbol{\theta}_{r,i}^U, \end{aligned} \tag{5.51}$$

where J_i is the cost to be minimized, \mathbf{W}_r is the $(H \times H)$ -dimensional weighting matrix, r_i is the rate of the i th reaction, which is a known function of the measured molar concentrations \mathbf{c}_l and the l -dimensional unknown parameter vector $\boldsymbol{\theta}_{r,i}$ that can vary between the bounds $\boldsymbol{\theta}_{r,i}^L$ and $\boldsymbol{\theta}_{r,i}^U$. Similarly, let $\hat{\mathbf{x}}_{m,l,j}$ and $\mathbf{x}_{m,l,j}$ denote the H -dimensional vectors of computed and simulated extents of the j th mass transfer in the liquid phase. The parameter estimation problem for the mass transfer rates can be formulated as:

$$\begin{aligned} \min_{\boldsymbol{\theta}_{m,j}} J_j &= (\hat{\mathbf{x}}_{m,l,j} - \mathbf{x}_{m,l,j}(\boldsymbol{\theta}_{m,j}))^T \mathbf{W}_m (\hat{\mathbf{x}}_{m,l,j} - \mathbf{x}_{m,l,j}(\boldsymbol{\theta}_{m,j})) \\ \text{s.t.} \quad \dot{\mathbf{x}}_{m,l,j}(t_h, \boldsymbol{\theta}_{m,j}) &= \zeta_j(\mathbf{c}_l(t_h), \mathbf{c}_g(t_h), \boldsymbol{\theta}_{m,j}) - \frac{u_{out,l}(t_h)}{m_l(t_h)} \mathbf{x}_{m,l,j}, \quad \mathbf{x}_{m,l,j}(0) = 0, \\ \boldsymbol{\theta}_{m,j}^L &\leq \boldsymbol{\theta}_{m,j} \leq \boldsymbol{\theta}_{m,j}^U, \end{aligned} \tag{5.52}$$

where J_j is the cost to be minimized, and ζ_j is the j th mass-transfer rate, which is a known function of both measured \mathbf{c}_l and \mathbf{c}_g and of the q -dimensional parameter vector $\boldsymbol{\theta}_{m,j}$ that can vary between the bounds $\boldsymbol{\theta}_{m,j}^L$ and $\boldsymbol{\theta}_{m,j}^U$, and \mathbf{W}_m is the $(H \times H)$ -dimensional weighting matrix.

Eq. (5.51) can be used to estimate the parameters of each reaction rate for homogeneous reaction systems and for G–L reaction systems. Eq. (5.52) can be used to estimate the parameters of each mass-transfer rate for G–L reaction systems. If only a subset of the concentrations is measured, the unmeasured concentrations can be reconstructed from the available measurements using Eq. (5.5) for homogeneous reactors, and Eqs. (5.13) and (5.12) for G–L reaction systems.

The rate expressions $r_i(\mathbf{c}_l, \boldsymbol{\theta}_{r,i})$ and $\zeta_j(\mathbf{c}_l, \mathbf{c}_g, \boldsymbol{\theta}_{m,j})$ are functions of \mathbf{c}_l and \mathbf{c}_g in addition to the parameters $\boldsymbol{\theta}$. Hence, integrating the differential equations of $x_{r,i}$ and $x_{m,l,j}$ requires the knowledge of the concentrations in the liquid and gas phases. To guarantee individual estimate of the rates, the noisy concentration measurements are directly used in Eqs. (5.51) and (5.52). Since noisy measurements are used to simulate the profiles for $x_{r,i}$ and $x_{m,l,j}$, error propagation can affect the accuracy of the estimated parameters.

5.4.3 Comparison of various incremental identification approaches

This section discusses the features of various incremental identification approaches available in the literature and the one proposed in this work. The incremental identification approaches using the differential method transform concentration measurements into individual reaction and mass-transfer rates, while those using the integral method transform concentration measurements into individual reaction and mass-transfer extents. Hence, the methods can be grouped into two categories: (i) extent-based methods, and (ii) rate-based methods. Some of these methods are compared in Table 5.2 for homogeneous reactions systems and in Table 5.3 for G–L reaction systems.

The first parts of Tables 5.2 and 5.3 give information regarding the required measured data, quantities that are computed from measured data (called computed data) and are required for the identification, and the required prior information. In a first data-transformation step, the extent- and rate-based methods isolate the contributions of each reaction and each mass transfer. For example, in Table 5.2, method R1 proceeds in two steps to compute the rate of the i th reaction via differentiation of $\tilde{\mathbf{n}}(t)^2$ and use of the measured inlet and outlet flowrates. Similarly, method V2 proceeds in two steps to compute the extent of the i th reaction using the available concentrations \mathbf{c}_a and integration of inlet and outlet flowrates. Then, the reaction and mass-transfer rates can be identified by solving a regression problem. For the extent-based methods, the regression problem involves a dynamic model as a constraint, while the regression problem for rate-based methods involves a static model. For example, in Table 5.2, method P2 involves a dynamic model of the extent of the i reaction.

Extent-based methods

Two types of extents of reaction and mass transfer are distinguished for extent-based methods: (i) the "overall" extents, and (ii) the "vessel" extents. The "vessel" extents of reaction and mass transfer are identical to the extents defined in Chapters 2 and 3. The "vessel" extents of the i th reaction and the j th mass transfer are given as follows:

$$\begin{aligned} \dot{x}_{r,i} &= V_l r_i - \frac{u_{out,l}}{m_l} x_{r,i}, & x_{r,i}(0) &= 0, \quad \forall i = 1, \dots, R, \\ \dot{x}_{m,l,j} &= \zeta_j - \frac{u_{out,l}}{m_l} x_{m,l,j}, & x_{m,l,j}(0) &= 0, \quad \forall j = 1, \dots, p_m. \end{aligned} \quad (5.53)$$

The "overall" extent of the i th reaction, $\xi_{r,i}$, represents the total number of moles produced by the i th reaction and can be expressed in terms of the rate of the i th reaction as follows:

$$\frac{d\xi_{r,i}}{dt} = V r_i, \quad \xi_{r,i}(0) = 0, \quad i = 1, \dots, R. \quad (5.54)$$

The "overall" extents of the j th mass transfer, $\xi_{m,j}$, represents the total number of moles transferred from the gas phase to the liquid phase by the j th mass transfer and can be expressed in terms of the rate of the j th mass transfer as follows:

² (\cdot) denotes the continuous approximation of discrete measurements

$$\frac{d\xi_{m,j}}{dt} = \zeta_j, \quad \xi_{m,j}(0) = 0, \quad j = 1, \dots, p_m. \quad (5.55)$$

The "overall" and "vessel" extents of reactions are identical for batch and semi-batch reactors because of the absence of the outlet flowrate. However, for continuous reactors, the "overall" and "vessel" extents of reactions are different.

These two types of extents lead to the three methods O1, V1 and V2. Method O1 allows computing the "overall" extents of each reaction and each mass transfer from the measured data, while methods V1 and V2 allow computing the "vessel" extents of reaction and mass transfer from measured data based on the approaches described in Section 5.1. Note that method V2 calls for the integration of high-resolution data, i.e. $\mathbf{u}_{in}(t)$ and $u_{out}(t)$. Method O1 can be combined with method P1 for the identification of a kinetic model. Similarly, methods V1 and V2 combine with method P2 and allow one to identify a kinetic model. The method P2 is based on the methods described in Section 5.4.2. The regression problem in method P1 is an adaptation of the estimation problems formulated in Section 5.4.2, where the dynamic models in Eqs. (5.54) and (5.55) are used as the constraints. Note that the extent-based methods are related to the *integral method* of kinetic identification.

Rate-based methods

The rate-based methods compute the reaction and mass-transfer rates through differentiation of either the reaction and mass-transfer fluxes or the extents of reaction and mass transfer. The reaction and mass-transfer fluxes for the various species are computed from the contributions of reaction and mass transfer in the total numbers of moles as follows:

- The contribution of reactions to the numbers of moles produced or consumed by the reactions at time t in homogeneous reaction systems, $\mathbf{d}(t)$, can be expressed in terms of the reaction fluxes (\mathbf{f}^r), which relate to the unknown reaction rates as $\mathbf{f}^r(t) = \mathbf{N}^T V(t) \mathbf{r}(t)$ as follows:

$$\mathbf{d}(t) := \int_0^t \mathbf{f}^r(\tau) d\tau = \int_0^t \mathbf{N}^T V(\tau) \mathbf{r}(\tau) d\tau. \quad (5.56)$$

Furthermore, $\hat{\mathbf{d}}(t)$ can also be computed from the change in the measured numbers of moles $\mathbf{n}(t) - \mathbf{n}_0$, by discounting the contributions of the inlet and outlet streams. Hence, one can write:

$$\hat{\mathbf{d}}(t) := \mathbf{n}(t) - \mathbf{n}_0 - \int_0^t \left(\mathbf{W}_{in} \mathbf{u}_{in}(\tau) - \frac{u_{out}(\tau)}{m(\tau)} \mathbf{n}(\tau) \right) d\tau, \quad (5.57)$$

where $(\hat{\cdot})$ indicates quantities computed from measurements.

- The contribution of reactions and mass transfers to the numbers of moles in the liquid phase at time t , $\mathbf{d}_l(t)$, can be expressed in terms of the reaction and mass-transfer fluxes \mathbf{f}_l^{rm} , which relate to the reaction rates \mathbf{r} and the mass-transfer rates $\boldsymbol{\zeta}$ as $\mathbf{f}_l^{rm} = \mathbf{N}^T V_l \mathbf{r} + \mathbf{W}_{m,l} \boldsymbol{\zeta}$ as:

$$\mathbf{d}_l(t) := \int_0^t \mathbf{f}_l^{rm}(\tau) d\tau = \int_0^t \left(\mathbf{N}^T V_l(\tau) \mathbf{r}(\tau) + \mathbf{W}_{m,l} \boldsymbol{\zeta}(\tau) \right) d\tau, \quad (5.58)$$

where \mathbf{f}_l^{rm} is the S_l -dimensional vector of reaction and mass-transfer fluxes. $\hat{\mathbf{d}}_l(t)$ can also be computed from the change in numbers of moles $\mathbf{n}_l(t) - \mathbf{n}_{l,0}$, by discounting the contributions of the liquid inlet and outlet streams as follows:

$$\hat{\mathbf{d}}_l(t) := \mathbf{n}_l(t) - \mathbf{n}_{l,0} - \int_0^t \left(\mathbf{W}_{in,l} \mathbf{u}_{in,l}(\tau) - \frac{u_{out,l}(\tau)}{m_l(\tau)} \mathbf{n}_l(\tau) \right) d\tau. \quad (5.59)$$

- Similarly, the contribution of mass transfers to the numbers of moles in the gas phase at time t , $\mathbf{d}_g(t)$, can be expressed in terms of the mass-transfer fluxes \mathbf{f}_g^m , which relate to the mass-transfer rates $\boldsymbol{\zeta}$ as $\mathbf{f}_g^m = -\mathbf{W}_{m,g} \boldsymbol{\zeta}$. Hence, one can write:

$$\mathbf{d}_g(t) := \int_0^t \mathbf{f}_g^m(\tau) d\tau = - \int_0^t \mathbf{W}_{m,g} \mathbf{x}_{m,g}(\tau) d\tau, \quad (5.60)$$

where \mathbf{f}_g^m is the S_g -dimensional vector of mass-transfer fluxes. Furthermore, $\hat{\mathbf{d}}_g(t)$ can also be computed from the change in numbers of moles $\mathbf{n}_g(t) - \mathbf{n}_{g,0}$, by discounting the contributions of the gas inlet and outlet streams as follows:

$$\hat{\mathbf{d}}_g(t) := \mathbf{n}_g(t) - \mathbf{n}_{g,0} - \int_0^t \left(\mathbf{W}_{in,g} \mathbf{u}_{in,g}(\tau) - \frac{u_{out,g}(\tau)}{m_g(\tau)} \mathbf{n}_g(\tau) \right) d\tau. \quad (5.61)$$

In G–L reaction systems, the fluxes \mathbf{f}_l^{rm} can be expressed as:

$$\mathbf{f}_l^{rm} = \mathbf{f}_l^r + \mathbf{f}_l^m = \left[\mathbf{N}^T \quad \mathbf{W}_{m,l} \right] \begin{bmatrix} V_l \mathbf{r} \\ \boldsymbol{\zeta} \end{bmatrix} = \mathbf{N}_{rm}^T \begin{bmatrix} V_l \mathbf{r} \\ \boldsymbol{\zeta} \end{bmatrix}, \quad (5.62)$$

where \mathbf{f}_l^r and \mathbf{f}_l^m are the S_l -dimensional vectors of reaction fluxes and mass-transfer fluxes, respectively. \mathbf{N}_{rm} is the $(R + p_m) \times S_l$ -dimensional extended stoichiometric matrix.

The fluxes \mathbf{f}_l^{rm} and \mathbf{f}_g^m can be combined as follows:

$$\mathbf{f}^t = \begin{bmatrix} \mathbf{f}_l^{rm} \\ \mathbf{f}_g^m \end{bmatrix} = \mathbf{N}_t^T \begin{bmatrix} V_l \mathbf{r} \\ \boldsymbol{\zeta} \end{bmatrix} = \begin{bmatrix} \mathbf{N}^T & \mathbf{W}_{m,l} \\ \mathbf{0}_{S_g \times R} & -\mathbf{W}_{m,g} \end{bmatrix} \begin{bmatrix} V_l \mathbf{r} \\ \boldsymbol{\zeta} \end{bmatrix}, \quad (5.63)$$

where \mathbf{f}^t is the $(S_l + S_g)$ -dimensional vector of reaction and mass-transfer fluxes in G–L reaction systems. Note that the mass-transfer rates can be computed from either gas or liquid measurements. \mathbf{N}_t is the $(R + p_m) \times (S_l + S_g)$ -dimensional total stoichiometric matrix.

The rate-based methods lead to methods R1, R2 and R3. Method R1 computes the reaction rates (or mass-transfer rates) through differentiation of the concentration data. Method R2 computes the reaction rates through differentiation of the total numbers of moles produced or consumed by the reactions and/or mass transfers (\mathbf{d} or \mathbf{d}_f , $f \in \{g, l\}$). In method R3, the rate of each reaction or each mass transfer is obtained individually via time differentiation of the corresponding computed extent. Then, the reaction kinetics can be identified through solving the regression problem with a static model formulated in method P3. Note that the rate-based methods are related to the *differential method* of kinetic identification.

Table 5.2 Comparison of incremental extent- and rate-based methods for the identification of kinetic models in homogeneous reaction systems

Measured data	$\mathbf{c}(t_h), V(t), \mathbf{u}_{in}(t), u_{out}(t) \quad (h = 0, 1, \dots, H)$
Computed data	$m(t) = m_0 + \int_0^t \left(\mathbf{1}_p^T \mathbf{u}_n(\tau) - u_{out}(\tau) \right) d\tau; \quad \mathbf{n}(t_h) = \mathbf{c}(t_h)V(t_h); \quad \tilde{\mathbf{c}}(t) = \sum_{h=0}^H \mathbf{c}(t_h)\phi_h(t); \quad \tilde{\mathbf{n}}(t) = \tilde{\mathbf{c}}(t)V(t)$
Prior information	$\mathbf{N}, \mathbf{W}_{in}$
Data transformation	<p>Extent-based methods</p> <p>Computation of "overall" extents of reaction</p> <p>O1. Via integration of $\tilde{\mathbf{n}}(t)$: $[\mathbf{n}(t_h), \mathbf{u}_{in}(t), u_{out}(t)] \rightarrow [\xi_i(t_h)]$ [15, 63]</p> <p>Step 1: Compute total numbers of moles produced or consumed by reactions:</p> $\mathbf{d}(t_h) := \mathbf{n}(t_h) - \mathbf{n}_0 - \int_0^{t_h} \left(\mathbf{W}_{in} \mathbf{u}_{in}(\tau) - \frac{u_{out}(\tau)}{m(\tau)} \tilde{\mathbf{n}}(\tau) \right) d\tau$ <p>Step 2: Compute "overall" extent of the ith reaction</p> $\xi_i(t_h) = (\mathbf{N}^T)_i^+ \mathbf{d}(t_h), \quad \xi_i(0) = 0$ <p>Computation of "vessel" extents of reaction</p> <p>V1. Linear transformation of $\mathbf{n}(t_h)$: $[\mathbf{n}(t_h)] \rightarrow [x_{r,i}(t_h)]$</p> <p>Step 1: Compute "vessel" extent of the ith reaction</p> $x_{r,i}(t_h) = (\mathbf{S}_0^T)_i \mathbf{n}(t_h), \quad x_{r,i}(0) = 0$ <p>V2. Use of $\mathbf{n}_a(t_h)$ and integration of $\mathbf{u}_{in}(t)$ and $u_{out}(t)$:</p> $[\mathbf{n}_a(t_h), \mathbf{u}_{in}(t), u_{out}(t)] \rightarrow [x_{r,i}(t_h)]$ <p>Step 1: Compute $\lambda(t)$ and $\mathbf{x}_{in}(t)$</p> $\dot{\lambda}(t) = -\frac{u_{out}(t)}{m(t)} \lambda(t), \quad \lambda(0) = 1$ $\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) - \frac{u_{out}(t)}{m(t)} \mathbf{x}_{in}(t), \quad \mathbf{x}_{in}(0) = 0$ <p>Step 2: Compute "vessel" extent of the ith reaction</p> $x_{r,i}(t_h) = (\mathbf{N}_a^T)_i^+ \left(\mathbf{n}_a(t_h) - \mathbf{W}_{in,k} \mathbf{x}_{in}(t_h) - \mathbf{n}_{0,k} \lambda(t_h) \right), \quad x_{r,i}(0) = 0$
	<p>Rate-based methods</p> <p>Computation of reaction rates</p> <p>R1. Via differentiation of $\tilde{\mathbf{n}}(t)$: $[\mathbf{n}(t_h), \mathbf{u}_{in}(t), u_{out}(t)] \rightarrow [r_i(t_h)]$ [1]</p> <p>Step 1: Compute reaction fluxes through differentiation of $\tilde{\mathbf{n}}(t)$</p> $\mathbf{f}^r(t_h) := \frac{d\tilde{\mathbf{n}}}{dt}(t_h) - \mathbf{W}_{in} \mathbf{u}_{in}(t_h) + \frac{u_{out}(t_h)}{m(t_h)} \tilde{\mathbf{n}}(t_h)$ <p>Step 2: Compute rate of the ith reaction</p> $r_i(t_h) = (\mathbf{N}^T)_i^+ \mathbf{f}^r(t_h) V^{-1}(t_h)$ <p>R2. Via integration of $\tilde{\mathbf{n}}(t)$ and differentiation of $\tilde{\mathbf{d}}(t)$:</p> $[\mathbf{n}(t_h), \mathbf{u}_{in}(t), u_{out}(t)] \rightarrow [r_i(t_h)] \quad [17]$ <p>Step 1: Compute total numbers of moles produced or consumed by reactions:</p> $\mathbf{d}(t_h) := \mathbf{n}(t_h) - \mathbf{n}_0 - \int_0^{t_h} \left(\mathbf{W}_{in} \mathbf{u}_{in}(\tau) - \frac{u_{out}(\tau)}{m(\tau)} \tilde{\mathbf{n}}(\tau) \right) d\tau$ <p>Step 2: Compute reaction fluxes through differentiation of $\mathbf{d}(t_h)$</p> $\mathbf{f}^r(t_h) := \frac{d\mathbf{d}}{dt}(t_h)$ <p>Step 3: Compute rate of the ith reaction</p> $r_i(t_h) = (\mathbf{N}^T)_i^+ \mathbf{f}^r(t_h) V^{-1}(t_h)$ <p>R3. Differentiation of $\tilde{x}_{r,i}(t)$: $[\mathbf{n}(t_h), \mathbf{u}_{in}(t), u_{out}(t)] \rightarrow [r_i(t_h)]$</p> <p>Step 1: $x_{r,i}(t_h)$ from V1 or V2; $\tilde{x}_{r,i}(t) = \sum_{h=0}^H x_{r,i}(t_h) \phi_h(t)$</p> <p>Step 2: Compute rate of the ith reaction through differentiation of $\tilde{x}_{r,i}(t)$</p> $r_i(t_h) = V^{-1}(t_h) \left(\frac{d\tilde{x}_{r,i}}{dt}(t_h) + \frac{u_{out}(t_h)}{m(t_h)} x_{r,i}(t_h) \right)$

Table 5.2 Comparison of incremental extent- and rate-based methods for the identification of kinetic models in homogeneous reaction systems (continued)

	<u>Identification of kinetic parameters</u> Regression problem involving a dynamic model P1. From "overall" extent $\xi_i(t_h)$; integration of $\tilde{c}(t)$ $\hat{\boldsymbol{\theta}}_i = \arg \min_{\boldsymbol{\theta}_i} \sum_{h=0}^H \left(\xi_i(t_h) - \xi_i(\boldsymbol{\theta}_i, t_h) \right)^2$ s.t. $\dot{\xi}_i(\boldsymbol{\theta}_i, t) = r_i(\tilde{c}(t), \boldsymbol{\theta}_i) V(t), \quad \xi_i(\boldsymbol{\theta}_i, 0) = 0,$ $\boldsymbol{\theta}_i^L \leq \boldsymbol{\theta}_i \leq \boldsymbol{\theta}_i^U$ P2. From "vessel" extent $x_{r,i}(t_h)$; integration of $\tilde{c}(t)$ $\hat{\boldsymbol{\theta}}_i = \arg \min_{\boldsymbol{\theta}_i} \sum_{h=0}^H \left(x_{r,i}(t_h) - x_{r,i}(\boldsymbol{\theta}_i, t_h) \right)^2$ s.t. $\dot{x}_{r,i}(\boldsymbol{\theta}_i, t) = r_i(\tilde{c}(t), \boldsymbol{\theta}_i) V(t) - \frac{u_{out,i}(t)}{m(t)} x_{r,i}(\boldsymbol{\theta}_i, t), \quad x_{r,i}(\boldsymbol{\theta}_i, 0) = 0,$ $\boldsymbol{\theta}_i^L \leq \boldsymbol{\theta}_i \leq \boldsymbol{\theta}_i^U$	<u>Identification of kinetic parameters</u> Regression problem involving a static model P3. From reaction rate $r_i(t_h)$ $\hat{\boldsymbol{\theta}}_i = \arg \min_{\boldsymbol{\theta}_i} \sum_{h=0}^{H-1} \left(r_i(t_h) - r_i(\mathbf{c}(t_h), \boldsymbol{\theta}_i) \right)^2$ $\boldsymbol{\theta}_i^L \leq \boldsymbol{\theta}_i \leq \boldsymbol{\theta}_i^U$
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Table 5.3 Comparison of incremental extent- and rate-based methods for the identification of kinetic models in G–L reaction systems

Measured data	$\mathbf{c}_f(t_h), m_f(t), V_l(t), \mathbf{u}_{in,f}(t), u_{out,f}(t),$ where $f \in \{l, g\}; h = 0, 1, \dots, H$	
Computed data	$V_g(t) = V_t - V_l(t); \mathbf{n}_f(t_h) = \mathbf{c}_f(t_h)V_f(t_h); \tilde{\mathbf{c}}_f(t) = \sum_{h=0}^H \mathbf{c}_f(t_h)\phi_{f,h}(t); \tilde{\mathbf{n}}_f(t) = \tilde{\mathbf{c}}_f(t)V_f(t)$	
Prior information	$\mathbf{N}, \mathbf{W}_{in,f}, \mathbf{W}_{m,f}$	
Data transformation	Extent-based methods	Rate-based methods
	Computation of "overall" extents of reaction and mass transfer <u>O1.</u> Via integration of $\tilde{\mathbf{n}}_f(t)$: $[\mathbf{n}_f(t_h), \mathbf{u}_{in,f}(t), u_{out,f}(t)]$ $\rightarrow [\xi_{r,i}(t_h), \xi_{m,j}(t_h)]$ <u>Step 1:</u> Compute total numbers of moles produced or consumed by reactions and mass transfers in the f phase: $\mathbf{d}_f(t_h) = \mathbf{n}_f(t_h) - \mathbf{n}_{f,0} - \int_0^{t_h} \left(\mathbf{W}_{in,f} \mathbf{u}_{in,f}(\tau) - \frac{u_{out,f}(\tau)}{m_f(\tau)} \tilde{\mathbf{n}}_f(\tau) \right) d\tau$ <u>Step 2:</u> Compute "overall" extent of the i th reaction and j th mass transfer from $\mathbf{d}_f(t_h)$: $\xi_{r,i}(t_h) = (\mathbf{N}_{rm}^T)_i^+ \mathbf{d}_i(t_h), \quad \xi_{r,i}(0) = 0, \quad i = 1, \dots, R$ $\xi_{m,j}(t_h) = (\mathbf{N}_{rm}^T)_{R+j}^+ \mathbf{d}_l(t_h) = -(\mathbf{W}_{m,g})_{j,j}^+ \mathbf{d}_g(t_h), \quad \xi_{m,j}(0) = 0, \quad j = 1, \dots, p_m$	Computation of reaction and mass-transfer rates <u>R1.</u> Via differentiation of $\tilde{\mathbf{n}}_f(t)$: $[\mathbf{n}_f(t_h), \mathbf{u}_{in,f}(t), u_{out,f}(t)]$ $\rightarrow [r_i(t_h), \zeta_j(t_h)]$ <u>Step 1:</u> Compute reaction and mass-transfer fluxes through differentiation of $\tilde{\mathbf{n}}_f(t)$: $\mathbf{f}_f^r(t_h) = \frac{d\tilde{\mathbf{n}}_f}{dt}(t_h) - \mathbf{W}_{in,f} \mathbf{u}_{in,f}(t_h) + \frac{u_{out,f}(t_h)}{m_f(t_h)} \tilde{\mathbf{n}}_f(t_h)$ <u>Step 2:</u> Compute rate of the i th reaction and j th mass transfer from the total fluxes, $\mathbf{f}^t = [\mathbf{f}_f^r]$: $r_i(t_h) = (\mathbf{N}_t^T)_i^+ \mathbf{f}^t(t_h) V_t^{-1}(t_h), \quad i = 1, \dots, R$ $\zeta_j(t_h) = (\mathbf{N}_t^T)_{R+j}^+ \mathbf{f}^t(t_h), \quad j = 1, \dots, p_m$
	Computation of "vessel" extents of reaction and mass transfer	Computation of $\tilde{\mathbf{d}}_f(t)$:
	<u>V1.</u> Linear transformation of $\mathbf{n}_l(t_h)$: $[\mathbf{n}_l(t_h)] \rightarrow [x_{r,i}(t_h), x_{m,i,j}(t_h)]$ <u>Step 1:</u> Compute "vessel" extent of the i th reaction and j th mass transfer in the liquid phase: $x_{r,i}(t_h) = (\mathbf{S}_0^T)_i \mathbf{n}_l(t_h), \quad x_{r,i}(0) = 0, \quad i = 1, \dots, R$ $x_{m,i,j}(t_h) = (\mathbf{M}_{m,10}^T)_j \mathbf{n}_l(t_h), \quad x_{m,i,j}(0) = 0, \quad j = 1, \dots, p_m$	<u>Step 1:</u> Compute numbers of moles produced or consumed by reactions and mass transfers in the f phase: $\mathbf{d}_f(t_h) = \mathbf{n}_f(t_h) - \mathbf{n}_{f,0} - \int_0^{t_h} \left(\mathbf{W}_{in,f} \mathbf{u}_{in,f}(\tau) - \frac{u_{out,f}(\tau)}{m_f(\tau)} \tilde{\mathbf{n}}_f(\tau) \right) d\tau$ <u>Step 2:</u> Compute reaction and mass fluxes through differentiation of $\tilde{\mathbf{d}}_f(t_h)$ $\tilde{\mathbf{d}}_f(t) = \sum_{h=0}^H \mathbf{d}_f(t_h) \phi_{f,h}(t); \mathbf{f}_f^r(t_h) = \frac{d\tilde{\mathbf{d}}_f}{dt}(t_h); \mathbf{f}_f^m(t_h) = \frac{d\tilde{\mathbf{d}}_g}{dt}(t_h)$

Table 5.3 Comparison of incremental extent- and rate-based methods for the identification of kinetic models in G–L reaction systems (continued)

Data transformation (cont.)	<p>V2. Use of $\mathbf{n}_{l,a}(t_h)$ and $\mathbf{n}_{g,a}(t_h)$ and integration of $\mathbf{u}_{in,f}(t)$ and $u_{out,f}(t)$:</p> $\frac{[\mathbf{n}_{l,a}(t_h), \mathbf{n}_{g,a}(t_h), \mathbf{u}_{in,f}(t), u_{out,f}(t)] \rightarrow [x_{r,i}(t_h), x_{m,i,j}(t_h)]}{\text{Step 1: Computation of extent of the } j\text{th mass transfer } x_{m,g,j} \text{ in the gas phase:}}$ $\dot{\mathbf{x}}_{in,g}(t) = \mathbf{u}_{in,g}(t) - \frac{u_{out,g}(t)}{m_g(t)} \mathbf{x}_{in,g}(t), \quad \mathbf{x}_{in,g}(0) = \mathbf{0}_{pg},$ $\dot{\lambda}_g(t) = -\frac{u_{out,g}(t)}{m_g(t)} \lambda_g, \quad \lambda_g(0) = 1,$ $x_{m,g,j}(t_h) = -(\mathbf{W}_{m,g,g,a})_j^+ \left((V_t - V_l(t_h)) \mathbf{n}_{g,a}(t_h) - \mathbf{W}_{in,g,a} \mathbf{x}_{in,g}(t_h) - \lambda_g(t_h) \mathbf{n}_{g0,a} \right)$ <p>where $j = 1, \dots, p_{mg}$.</p> <p>Step 2: Computation of extent of the jth mass transfer $x_{m,g,i,j}$ in the liquid phase:</p> $\dot{\phi}_j(t) = -\frac{u_{out,l}(t)}{m_l(t)} \phi_j(t) + \left(\frac{u_{out,g}(t)}{m_g(t)} - \frac{u_{out,l}(t)}{m_g(t)} \right) x_{m,g,j}(t), \quad \phi_j(0) = 0,$ $x_{m,g,i,j}(t_h) = x_{m,g,j}(t_h) - \phi_j(t_h)$	<p>Step 3: Compute rate of the ith reaction and the jth mass transfer from $\mathbf{f}_l^m(t_h)$ and $\mathbf{f}_g^m(t_h)$:</p> $r_i(t_h) = (\mathbf{N}_{rm}^T)_i^+ \mathbf{f}_l^m(t_h) V_l^{-1}(t_h)$ $\zeta_j(t_h) = (\mathbf{N}_{rm}^T)_{R+j}^+ \mathbf{f}_l^m(t_h) = -(\mathbf{W}_{m,g})_j^+ \mathbf{f}_g^m$ <p>where $i = 1, \dots, R$ and $j = 1, \dots, p_m$</p> <p>R3. Via differentiation of $\tilde{x}_{r,i}(t)$ and $\tilde{x}_{m,i,j}(t)$:</p> $\frac{[\mathbf{n}_f(t_h), \mathbf{u}_{in,f}(t), u_{out,f}(t)] \rightarrow [r_i(t_h), \zeta_j(t_h)]}{\text{Step 1: Compute the extents } x_{r,i}(t_h) \text{ and } x_{m,i,j}(t) \text{ from V1 or V2; } \tilde{x}_{r,i}(t) = \sum_{h=0}^H x_{r,i}(t_h) \phi_h(t); \tilde{x}_{m,i,j}(t) = \sum_{h=0}^H x_{m,i,j}(t_h) \phi_h(t); \tilde{x}_{m,g,j}(t) = \sum_{h=0}^H x_{m,g,j}(t_h) \phi_h(t)}$ <p>Step 2: Compute rate of the ith reaction and the jth mass transfer through differentiation of $\tilde{x}_{r,i}(t)$ and $\tilde{x}_{m,i,j}(t)$ (or $\tilde{x}_{m,g,j}(t)$):</p> $r_i(t_h) = V_l^{-1}(t_h) \left(\frac{d\tilde{x}_{r,i}}{dt}(t_h) + \frac{u_{out,l}(t_h)}{m_l(t_h)} \tilde{x}_{r,i}(t_h) \right)$ $\zeta_j(t_h) = \frac{d\tilde{x}_{m,i,j}}{dt}(t_h) + \frac{u_{out,l}(t_h)}{m_l(t_h)} \tilde{x}_{m,i,j}(t_h)$ $= \frac{d\tilde{x}_{m,g,j}}{dt}(t_h) + \frac{u_{out,g}(t_h)}{m_g(t_h)} \tilde{x}_{m,g,j}(t_h)$ <p>where $i = 1, \dots, R$ and $j = 1, \dots, p_m$</p>
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Table 5.3 Comparison of incremental extent- and rate-based methods for the identification of kinetic models in G–L reaction systems (continued)

	Identification of kinetic parameters	Identification of kinetic parameters
Identification of kinetic models	<p>Regression problem involving a <i>dynamic model</i></p> <p>P1. From "overall" extent $\xi_{r,i}(t_h)$ and $\xi_{m,j}(t_h)$; integration of $\tilde{\mathbf{c}}_l(t)$ and $\tilde{\mathbf{c}}_g(t)$</p> <p>P1a: Estimation of $\boldsymbol{\theta}_i$ from $\xi_{r,i}(t_h)$:</p> $\hat{\boldsymbol{\theta}}_i = \arg \min_{\boldsymbol{\theta}_i} \sum_{h=0}^H \left(\xi_{r,i}(t_h) - \xi_{r,i}(\boldsymbol{\theta}_i, t_h) \right)^2$ <p>s.t. $\dot{\xi}_{r,i}(\boldsymbol{\theta}_i, t) = r_i(\tilde{\mathbf{c}}_l(t), \boldsymbol{\theta}_i) V_l(t), \quad \xi_{r,i}(\boldsymbol{\theta}_i, 0) = 0,$</p> $\boldsymbol{\theta}_i^L \leq \boldsymbol{\theta}_i \leq \boldsymbol{\theta}_i^U$	<p>Regression problem involving a <i>static model</i></p> <p>P3. From reaction rate $r_i(t_h)$ and mass-transfer rate $\zeta_j(t_h)$</p> <p>P3a: Estimation of $\boldsymbol{\theta}_i$ from $r_i(t_h)$:</p> $\hat{\boldsymbol{\theta}}_i = \arg \min_{\boldsymbol{\theta}_i} \sum_{h=0}^{H-1} \left(r_i(t_h) - r_i(\mathbf{c}_l(t_h), \boldsymbol{\theta}_i) \right)^2$ $\boldsymbol{\theta}_i^L \leq \boldsymbol{\theta}_i \leq \boldsymbol{\theta}_i^U$
	<p>P1b: Estimation of $\boldsymbol{\theta}_j$ from $\xi_{m,j}(t_h)$:</p> $\hat{\boldsymbol{\theta}}_j = \arg \min_{\boldsymbol{\theta}_j} \sum_{h=0}^H \left(\xi_{m,j}(t_h) - \xi_{m,j}(\boldsymbol{\theta}_j, t_h) \right)^2$ <p>s.t. $\dot{\xi}_{m,j}(\boldsymbol{\theta}_j, t) = \zeta_j(\tilde{\mathbf{c}}_l(t), \tilde{\mathbf{c}}_g, \boldsymbol{\theta}_j), \quad \xi_{m,j}(\boldsymbol{\theta}_j, 0) = 0,$</p> $\boldsymbol{\theta}_j^L \leq \boldsymbol{\theta}_j \leq \boldsymbol{\theta}_j^U$	<p>P3b: Estimation of $\boldsymbol{\theta}_j$ from $\zeta_j(t_h)$:</p> $\hat{\boldsymbol{\theta}}_j = \arg \min_{\boldsymbol{\theta}_j} \sum_{h=0}^{H-1} \left(\zeta_j(t_h) - \zeta_j(\mathbf{c}_l(t_h), \mathbf{c}_g(t_h), \boldsymbol{\theta}_j) \right)^2$ $\boldsymbol{\theta}_j^L \leq \boldsymbol{\theta}_j \leq \boldsymbol{\theta}_j^U$
	<p>P2. From "vessel" extents $x_{r,i}(t_h)$ and $x_{m,i,j}(t_h)$; integration of $\tilde{\mathbf{c}}_l(t)$, $\tilde{\mathbf{c}}_g(t)$</p> <p>P2a: Estimation of $\boldsymbol{\theta}_i$ from $x_{r,i}(t_h)$:</p> $\hat{\boldsymbol{\theta}}_i = \arg \min_{\boldsymbol{\theta}_i} \sum_{h=0}^H \left(x_{r,i}(t_h) - x_{r,i}(\boldsymbol{\theta}_i, t_h) \right)^2$ <p>s.t. $\dot{x}_{r,i}(\boldsymbol{\theta}_i, t) = r_i(\tilde{\mathbf{c}}_l(t), \boldsymbol{\theta}_i) V_l(t) - \frac{u_{out,i}(t)}{m_l(t)} x_{r,i}(\boldsymbol{\theta}_i, t), \quad x_{r,i}(\boldsymbol{\theta}_i, 0) = 0,$</p> $\boldsymbol{\theta}_i^L \leq \boldsymbol{\theta}_i \leq \boldsymbol{\theta}_i^U$	
	<p>P2b: Estimation of $\boldsymbol{\theta}_j$ from $x_{m,i,j}(t_h)$:</p> $\hat{\boldsymbol{\theta}}_j = \arg \min_{\boldsymbol{\theta}_j} \sum_{h=0}^H \left(x_{m,i,j}(t_h) - x_{m,i,j}(\boldsymbol{\theta}_j, t_h) \right)^2$ <p>s.t. $\dot{x}_{m,i,j}(\boldsymbol{\theta}_j, t) = \zeta_j(\tilde{\mathbf{c}}_l(t), \tilde{\mathbf{c}}_g(t), \boldsymbol{\theta}_j) - \frac{u_{out,i}(t)}{m_l(t)} x_{m,i,j}(\boldsymbol{\theta}_j, t), \quad x_{m,i,j}(\boldsymbol{\theta}_j, 0) = 0,$</p> $\boldsymbol{\theta}_j^L \leq \boldsymbol{\theta}_j \leq \boldsymbol{\theta}_j^U$	

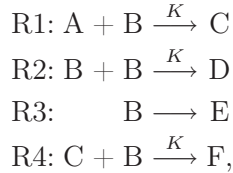
5.5 Illustrative simulated examples

The computation of extents of reaction and mass transfer and the identification of reaction and mass-transfer rates are illustrated next based on simulated concentration measurements from homogeneous and gas–liquid reaction systems. The rank augmentation of spectral data using the gas consumption data is also illustrated for G–L reaction system. The acetoacetylation of pyrrole is considered as a homogeneous reaction system, while the chlorination of butanoic acid is considered as a G–L reaction system continued from Section 3.3.

5.5.1 Homogeneous reaction system: Identification of the acetoacetylation of pyrrole from measured concentrations

Generation of simulated data:

The acetoacetylation of pyrrole (A) with diketene (B) involves one main reaction and three side reactions. [70] The main reaction (R1) between pyrrole and diketene produces 2-acetoacetyl pyrrole (C). The side reactions include (R2), the dimerization of diketene to dehydroacetic acid (D); (R3), the oligomerization of diketene to oligomers (E); and (R4), a consecutive reaction between diketene and 2-acetoacetyl pyrrole to the by-product F. The reactions R1, R2 and R4 are catalyzed by pyridine (K). The reaction stoichiometry reads:



from which one can write the stoichiometric matrix \mathbf{N} :

$$\mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 0 & 0 & 0 \\ 0 & -2 & 0 & 1 & 0 & 0 \\ 0 & -1 & 0 & 0 & 1 & 0 \\ 0 & -1 & -1 & 0 & 0 & 1 \end{bmatrix}. \quad (5.64)$$

The kinetic expressions are as follows:

$$\begin{aligned} r_1 &= k_1 c_A c_B c_K \\ r_2 &= k_2 c_B^2 c_K \\ r_3 &= k_3 c_B \\ r_4 &= k_4 c_C c_B c_K, \end{aligned} \quad (5.65)$$

with the true parameter values used for the data generation given in the 2nd column of Table 5.5.[70]

The startup of an isothermal CSTR is considered. The initial concentrations of the 6 species are $\mathbf{c}_0 = [0.3 \ 1 \ 0.1 \ 0.01 \ 0 \ 0]^T \text{ mol L}^{-1}$. The species A and B are added continuously through one inlet with composition $\mathbf{c}_{in} = [2 \ 3.5 \ 0 \ 0 \ 0 \ 0]^T \text{ mol L}^{-1}$. The volumetric inlet flowrate is $q_{in} = 0.1 \text{ L min}^{-1}$. Under the assumption of constant density, the volumetric outlet flowrate is $q_{out} = 0.1 \text{ L min}^{-1}$. The volume of the reaction mixture is 1 L. There is initially 0.5 mol of catalyst in the reactor. The concentrations of all species are measured every 30 sec for 1 h. The measurements are corrupted with additive zero-mean Gaussian noise. The standard deviation for each species is taken as 5% of the maximum concentration of that species, i.e. $\sigma_s = 0.05 c_s^{max}$ for $s = \{A, B, C, D, E, F\}$. The noisy concentration measurements are shown in Figure 5.2.

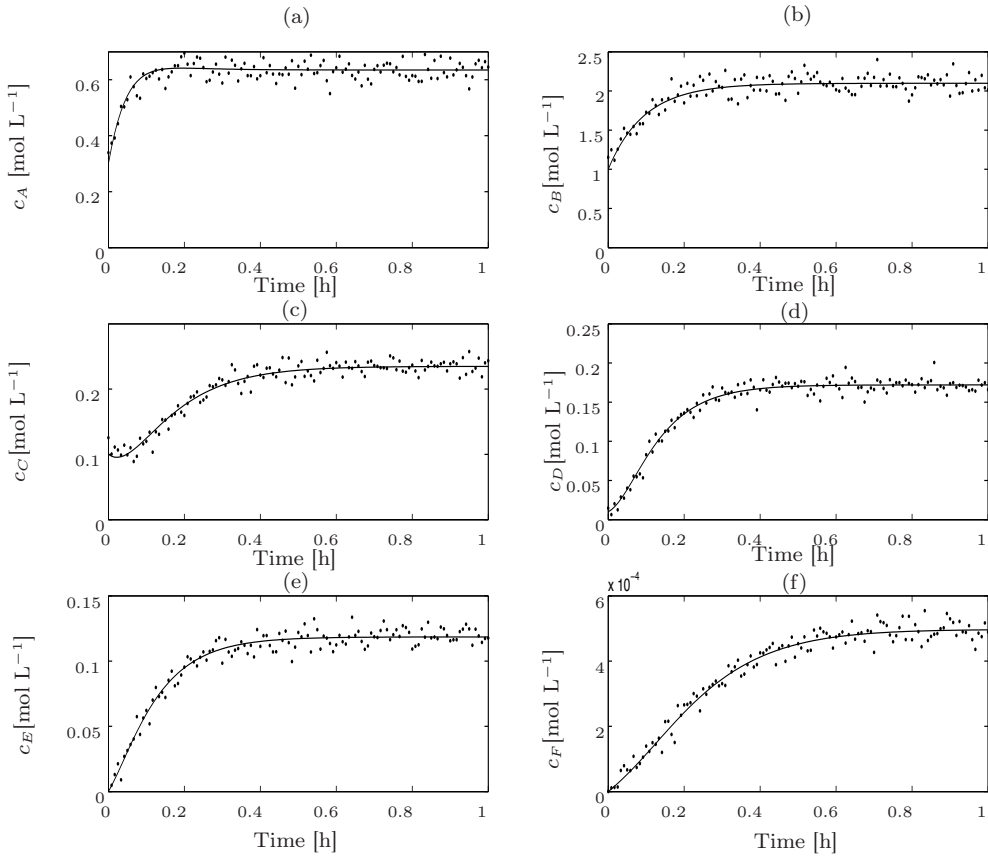


Figure 5.2 Concentrations of the 6 species in the acetoacetylation of pyrrole. The solid lines indicate the generated (true) concentrations, while the markers indicate the noisy measurements.

Identification of rate expressions:

Since the concentrations of all species are measured and $\text{rank}([\mathbf{N}^T \ \mathbf{c}_{in} \ \mathbf{n}_0]) = R + p + 1 = 4 + 1 + 1 = 6$, Corollary 5.1 can be used to compute the extents of reaction from concentration data. The computed extents, shown in Figure 5.3, are within the 95% confidence intervals computed using the information of the noise variance used for data generation.

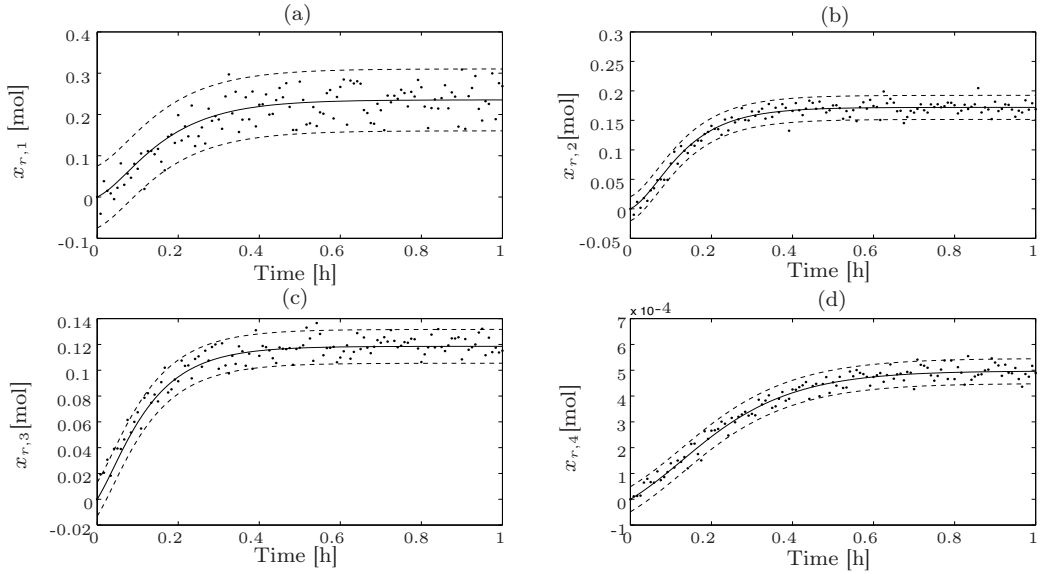


Figure 5.3 Extents of (a) reaction R1, (b) reaction R2, (c) reaction R3, and (d) reaction R4 computed from measured concentrations. The solid lines indicate the true extents, while the markers indicate the extents computed from noisy concentration measurements. The dash lines indicate the 95% confidence intervals.

The next step is to identify the rate expressions from among the set of rate candidates given for each reaction in Table 5.4. Note that each kinetic expression involves a single unknown parameter and thus $\theta_{r,1} = k_1$, $\theta_{r,2} = k_2$, $\theta_{r,3} = k_3$, and $\theta_{r,4} = k_4$. For each reaction, each candidate rate expression is fitted to the corresponding computed extent using the estimation problem (5.51). For example, for the main reaction R1, the quality of fit of rate expression candidates (4), (6), and (8) is shown in Figure 5.4. Fitting $r_1^{(8)}$ leads to the lowest least square cost for $\mathbf{W}_r = \mathbf{I}_H$. Similarly, the rate expressions $r_2^{(8)}$, $r_3^{(2)}$ and $r_4^{(6)}$ are identified as the suitable rate expressions of reactions R2, R3, and R4, which are indeed the rate expressions used for generating the data. The true values, the initial guesses, the estimated values and their 99% confidence intervals are given in Table 5.5. The estimated values are close to the true values.

Table 5.4 Rate expression candidates for the acetoacetylation of pyrrole. Candidates $r_1^{(8)}$, $r_2^{(5)}$, $r_3^{(2)}$ and $r_4^{(6)}$ correspond to the true rate expressions

Reaction R1:	Reaction R2:	Reaction R3:	Reaction R4:
$r_1^{(1)} = k_1$	$r_2^{(1)} = k_2$	$r_3^{(1)} = k_3$	$r_4^{(1)} = k_4$
$r_1^{(2)} = k_1 c_B$	$r_2^{(2)} = k_2 c_B$	$r_3^{(2)} = k_3 c_B$	$r_4^{(2)} = k_4 c_B$
$r_1^{(3)} = k_1 c_A$	$r_2^{(3)} = k_2 c_B^2$	$r_3^{(3)} = k_3 c_B^2$	$r_4^{(3)} = k_4 c_C$
$r_1^{(4)} = k_1 c_K$	$r_2^{(4)} = k_2 c_B c_K$	$r_3^{(4)} = k_3 c_B c_K$	$r_4^{(4)} = k_4 c_K$
$r_1^{(5)} = k_1 c_A c_B$	$r_2^{(5)} = k_2 c_B^2 c_K$	$r_3^{(5)} = k_3 c_B^2 c_K$	$r_4^{(5)} = k_4 c_B c_C$
$r_1^{(6)} = k_1 c_A c_K$	$r_2^{(6)} = k_2 c_K$	$r_3^{(6)} = k_3 c_K$	$r_4^{(6)} = k_4 c_K c_B c_C$
$r_1^{(7)} = k_1 c_B c_K$			$r_4^{(7)} = k_4 c_K c_B$
$r_1^{(8)} = k_1 c_A c_B c_K$			$r_4^{(8)} = k_4 c_K c_C$
$r_1^{(9)} = k_1 c_A^2 c_B$			$r_4^{(9)} = k_4 c_K c_B c_C^2$
$r_1^{(10)} = k_1 c_A c_B^2$			$r_4^{(10)} = k_4 c_K c_B^2 c_C$

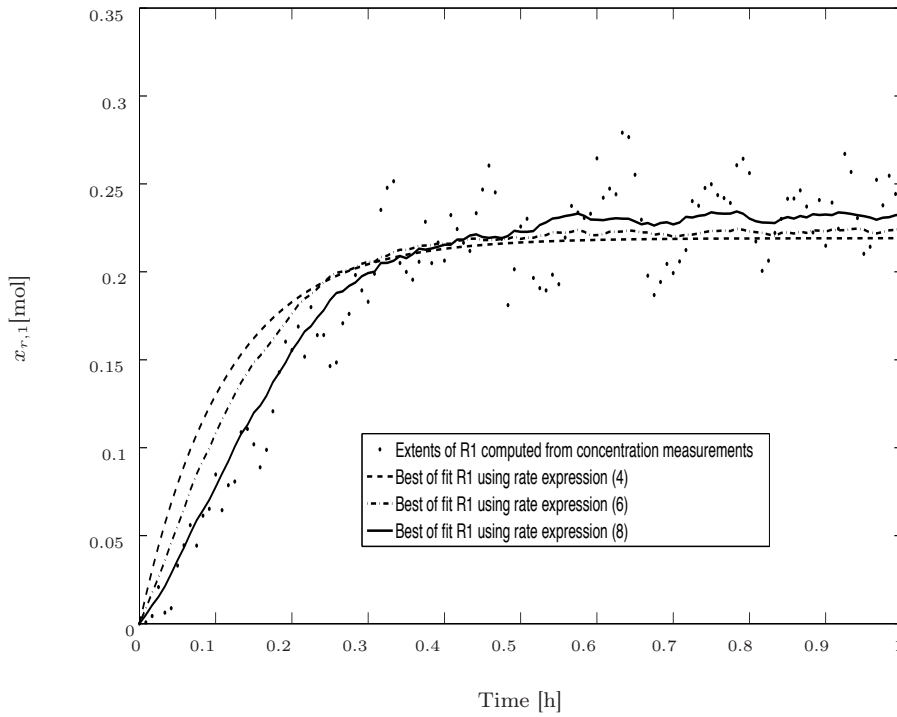


Figure 5.4 Fit of three rate expressions to the computed extent for R1.

Table 5.5 Parameter estimation using the integral method: True, initial and estimated values of the four kinetic parameters for the selected rate expressions $r_1^{(6)}$, $r_2^{(5)}$, $r_3^{(2)}$, and $r_4^{(6)}$. The last column indicates the 99% confidence interval for the estimated parameters.

Parameter	True value	Initial value	Estimated value	Confidence interval
k_1 [$\text{L}^2 \text{ mol}^{-2} \text{ min}^{-1}$]	0.0530	0.8000	0.0532	[0.0515, 0.0550]
k_2 [$\text{L}^2 \text{ mol}^{-2} \text{ min}^{-1}$]	0.1280	0.8000	0.1287	[0.1272, 0.1301]
k_3 [L min^{-1}]	0.0280	0.8000	0.0281	[0.0278, 0.0284]
k_4 [$\text{L}^2 \text{ mol}^{-2} \text{ min}^{-1}$]	0.0010	0.8000	0.0010	[0.0009, 0.0011]

5.5.2 Gas–liquid reaction system: Identification of the chlorination of butanoic acid from measured concentration data

Generation of simulated data:

The chlorination of butanoic acid (BA) described in Section 3.3 is considered as a G-L reaction system with the simplified kinetic expressions:

$$\begin{aligned} r_1 &= k_3 c_{l,BA} c_{l,Cl_2} \sqrt{c_{l,MBA}}, \\ r_2 &= k_4 r_1 c_{l,Cl_2}. \end{aligned} \quad (5.66)$$

The values of the rate constants are given in Table 5.7. The mass-transfer rates (in kg s^{-1}) are calculated using the following equations:

$$\begin{aligned} \zeta_{gl,Cl_2} &= k_{Cl_2} A_s V_l M_{w,Cl_2} (c_{Cl_2}^* - c_{l,Cl_2}), \quad c_{Cl_2}^* = \mathcal{P}_{Cl_2}/H_{Cl_2}, \\ \zeta_{lg,HCl} &= k_{HCl} A_s V_l M_{w,HCl} (c_{l,HCl} - c_{HCl}^*), \quad c_{HCl}^* = \mathcal{P}_{HCl}/H_{HCl}, \end{aligned} \quad (5.67)$$

where A is the specific interfacial area, $c_{Cl_2}^*$ and c_{HCl}^* are the equilibrium molar concentrations at the interface, c_{l,Cl_2} and $c_{l,HCl}$ are the molar concentrations in the liquid bulk, H_{Cl_2} and H_{HCl} are Henry's law constants, \mathcal{P}_{Cl_2} and \mathcal{P}_{HCl} are the partial pressures in the gas phase and are calculated using the ideal gas law from the numbers of moles in the gas phase.

The measurements are generated by simulating the chlorination of butanoic acid with inlet and outlet flows for an operation of 5 h. The initial pressure in the reactor is at 1 atm. The total pressure is regulated at 10 atm by manipulating the inlet flowrate of Cl_2 as shown in Figure 5.5d. The gaseous outlet flowrate $u_{out,g}$ is constant at 3600 kg h^{-1} . The liquid inlet flowrate of BA $u_{in,BA}$ is 324 kg h^{-1} , while the liquid outlet flow $u_{out,l}$ is manipulated to regulate the total mass of the liquid at 483 kg as shown in Figure 5.5b. It is assumed that the concentration measurements of Cl_2 , BA and MBA in the liquid phase ($S_{l,a} = 3$) and HCl ($S_{g,a} = 1$) in the gas phase are available. They are corrupted

with additive zero-mean Gaussian noise having a noise standard deviation of 2% of the maximum concentration of the corresponding species.

Identification of rate expressions of reactions and mass transfers

The liquid volume, and the inlet flowrate of Cl_2 , the liquid outlet flowrate, and the total pressure are measured (see Figure 5.5). The measured concentrations and numbers of moles are shown in Figure 5.6. Since the reactions R1 and R2 are autocatalytic, they start slowly because of the small amount of MBA initially present in the reactor. This leads to accumulation of Cl_2 and BA in the liquid phase (see Figure 5.6a-b). After about 0.15 h, the rates of both reactions increase, which leads to a sharp decrease in the amount of Cl_2 in the liquid phase. The amount of BA in the liquid phase decreases momentarily to increase later since the amount of BA added by the liquid inlet surpasses its removal due to the reactions and the liquid outlet. Moreover, the behavior of $n_{g,\text{HCl}}$ in Figure 5.6d indicates that the gas phase has reached near steady state after 0.2 h. The extended inlet-composition matrices $\bar{\mathbf{W}}_{in,g}$ and $\bar{\mathbf{W}}_{in,l}$ are given in Eqs. (3.42) and (3.43).

The stoichiometric and inlet-composition matrices corresponding to the measured quantities are as follows:

$$\mathbf{N}_a = \begin{bmatrix} -1 & -1 & 1 \\ -2 & -1 & 0 \end{bmatrix}; \quad \mathbf{W}_{m_l,l,a} = \begin{bmatrix} 0 & 0.0141 & 0 \end{bmatrix}; \quad \mathbf{N}_e = \begin{bmatrix} \mathbf{N}_a^T : \mathbf{W}_{m_l,l,a} \end{bmatrix};$$

$$\mathbf{W}_{m_g,g,a} = \begin{bmatrix} -0.0274 \end{bmatrix}; \quad \mathbf{W}_{in,g,a} = 0; \quad \mathbf{W}_{m_g,l,a} = \begin{bmatrix} 0.0274 \end{bmatrix} \quad \mathbf{W}_{in,l,a} = \begin{bmatrix} 0.0113 \end{bmatrix}.$$

The measurements satisfy Conditions (i)-(iii) in Proposition 5.1. Hence, the extents of the reactions R1 ($x_{r,1}$) and R2 ($x_{r,2}$) and the extents of mass transfer for Cl_2 (x_{m,l,Cl_2}) and HCl ($x_{m,g,\text{HCl}}$) can be computed from measurements as mentioned in Proposition 5.1. The plots of the computed extents are shown in Figure 5.7. The small value of $x_{r,2}$ indicates that the rate of the reaction R2 is smaller than that of the reaction R1 (Figure 5.7a-b). Since HCl transfers from the liquid to the gas, $x_{m,g,\text{HCl}}$ is negative and, furthermore, it is nearly constant after 0.2 h because of near steady-state condition in the gas phase (Figure 5.7c). The mass-transfer extent x_{m,l,Cl_2} increases with time because of the large driving force maintained by the consumption of Cl_2 in the reactions. The number of moles of Cl_2 in the gas phase and the concentration of HCl in the liquid phase are reconstructed from the available measurements using Eqs. (5.16) and (5.17) and shown in Figure 5.8. Note that these reconstructed quantities are required for parameter estimation.

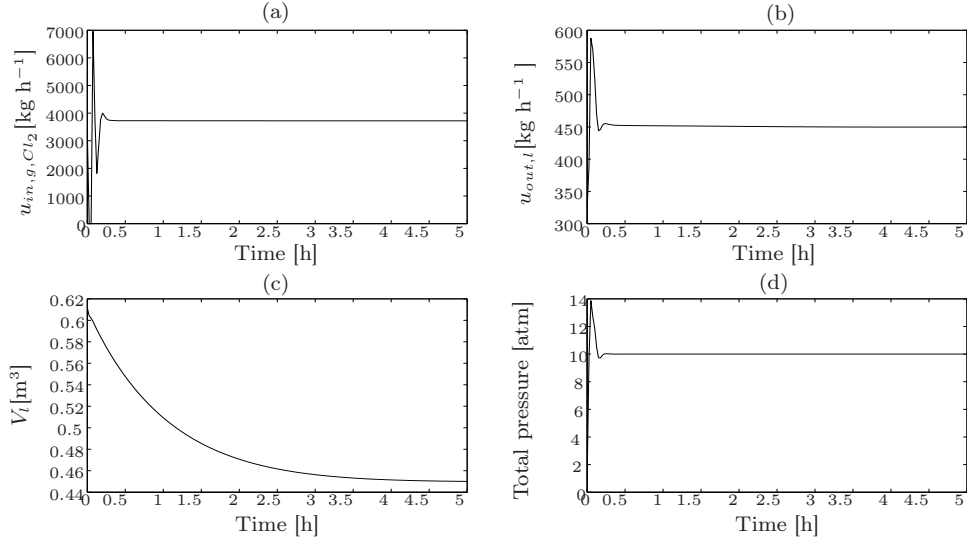


Figure 5.5 Chlorination of butanoic acid. Measured mass flowrates, volume of liquid phase and total pressure: (a) Inlet flowrate of Cl_2 in the gas phase, (b) outlet flowrate in the liquid phase, and (c) liquid volume, and (d) total pressure in the gas phase.

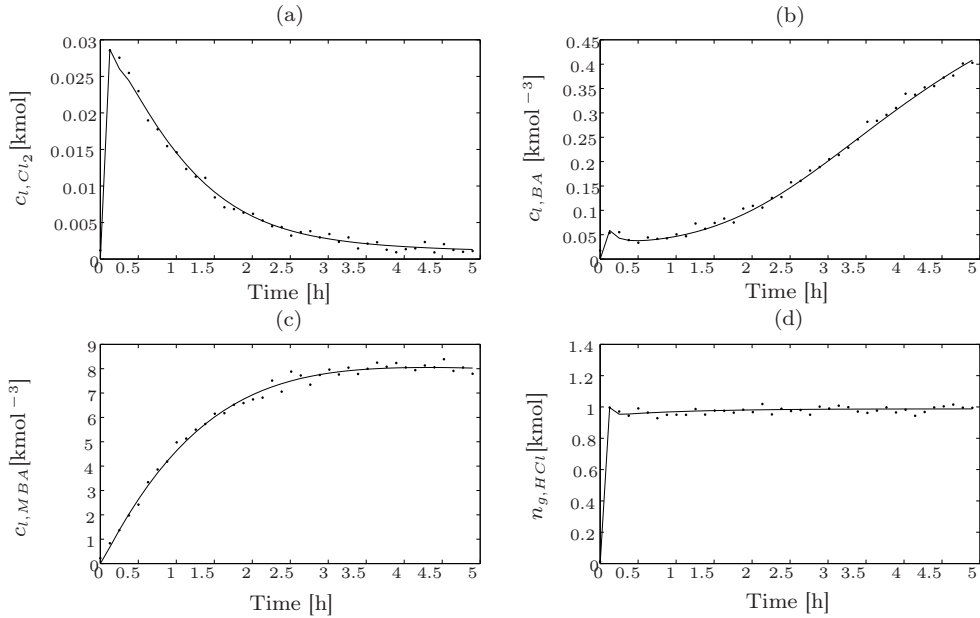


Figure 5.6 Chlorination of butanoic acid: (a) Concentration of Cl_2 in the liquid phase (c_{l,Cl_2}), (b) concentration of BA in the liquid phase ($c_{l,\text{BA}}$), and (c) concentration of MBA ($c_{l,\text{MBA}}$) in the liquid phase; (d) number of moles HCl in the gas phase. The solid lines indicate the true concentrations, while the markers indicate the noisy measured concentrations.

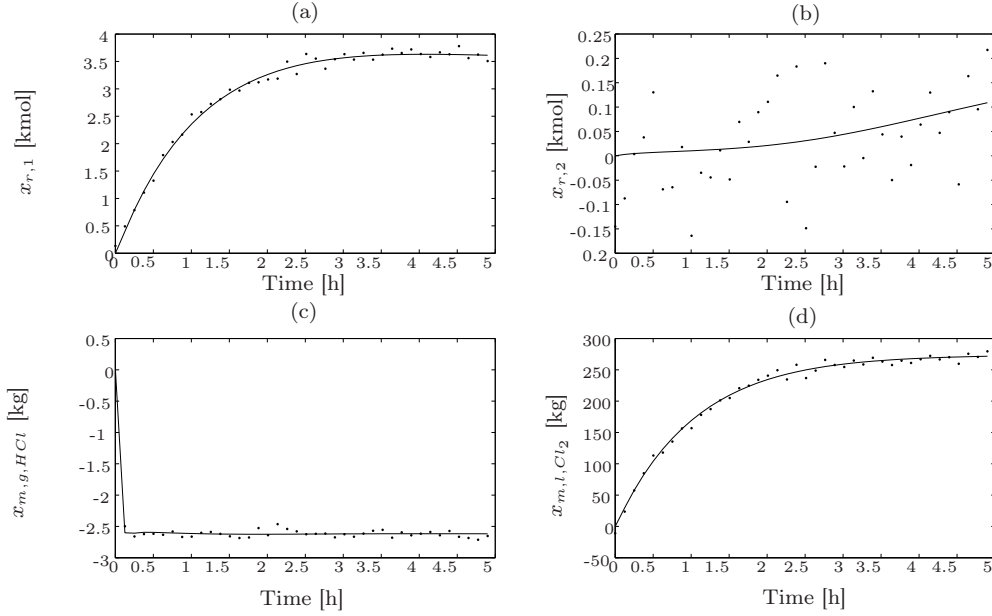


Figure 5.7 Chlorination of butanoic acid: (a) Extent of R1, (b) extent of R2, (c) extent of HCl mass transfer in the gas phase, and (d) extent of Cl₂ mass transfer to the liquid phase. The solid lines indicate the true extents of reaction and mass transfer, while the markers indicate the extents of reaction and mass transfer computed from the noisy measured concentrations.

Table 5.6 Reaction rate expression candidates for the chlorination of butanoic acid. Candidates $r_1^{(4)}$ and $r_2^{(4)}$ correspond to the true reaction rate expressions.

Reaction R1:	Reaction R2:
$r_1^{(1)} = k_1 c_{l,BA} c_{l,Cl_2}$	$r_1^{(1)} = k_2 c_{l,BA} c_{l,Cl_2}^2$
$r_1^{(2)} = k_1 c_{l,Cl_2}$	$r_2^{(2)} = k_2 c_{l,BA} c_{l,Cl_2}$
$r_1^{(3)} = k_1 c_{l,BA} c_{l,Cl_2} c_{l,MBA}$	$r_2^{(3)} = k_1 k_2 c_{l,BA} c_{l,Cl_2}^2 c_{l,MBA}$
$r_1^{(4)} = k_1 c_{l,BA} c_{l,Cl_2} \sqrt{c_{l,MBA}}$	$r_2^{(4)} = k_2 k_1 c_{l,BA} c_{l,Cl_2} \sqrt{c_{l,MBA}}$

The next step is to identify the reaction rate expressions from the set of rate expression candidates in Table 5.6. Note that the candidates $r_1^{(4)}$ and $r_2^{(4)}$ correspond to the true rate expressions. It will be assumed in this example that the structures of the mass-transfer rates are known. Additional mass-transfer rate expressions could be found elsewhere [87]. For each reaction, each candidate rate expression is fitted to the corresponding computed extent using the estimation problem (5.51). For the main reaction R1, the quality of fit of rate expression candidates (1), (2), (3), and (4) is shown in Figure 5.9. Fitting $r_1^{(4)}$ leads to the lowest least square cost for $\mathbf{W}_r = \mathbf{I}_H$. Similarly, for the side reaction R2, The rate expression $r_2^{(4)}$ is found suitable. The identified rate

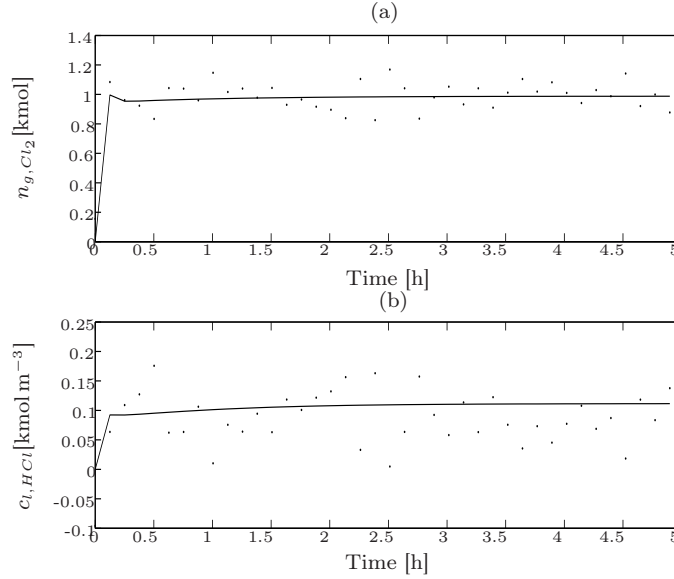


Figure 5.8 Chlorination of butanoic acid: (a) Number of moles of Cl_2 (n_{g,Cl_2}) in the gas phase, and (b) concentration of HCl ($c_{l,\text{HCl}}$) in the liquid phase. The solid line indicates the true concentration and numbers of moles, while the marker indicates the reconstructed concentration and numbers of moles.

Table 5.7 Parameter estimation using the integral method: True, initial and estimated values of the two reaction rate and the two mass-transfer rate parameters. The last column indicates the 99% confidence interval for the estimated parameters.

Parameter	True value	Initial value	Estimated value	Confidence interval
k_1 [m ³ kmol ⁻¹]	1.3577	0.8000	1.3543	[1.3207, 1.3879]
k_2 [-]	0.1	0.0200	0.105	[0.0884, 0.1216]
k_{Cl_2} [m s ⁻¹]	0.666×10^{-4}	0.0002	0.594×10^{-4}	$[0.514 \times 10^{-4}, 0.674 \times 10^{-4}]$
k_{HCl} [m s ⁻¹]	0.845×10^{-4}	0.0002	0.813×10^{-4}	$[0.762 \times 10^{-4}, 0.863 \times 10^{-4}]$

expressions correspond to the rate expressions used for generating the data. The true values, the initial guesses, the estimated values and their 99% confidence intervals are given in Table 5.7. True and estimated values are very close to each other.

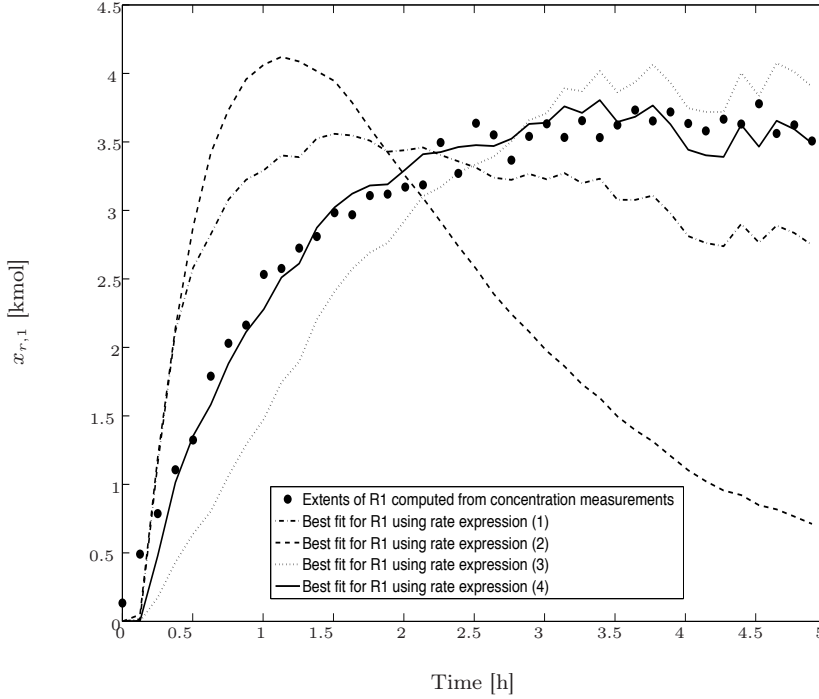


Figure 5.9 Fit of three rate expressions to the computed extent for R1.

5.5.3 Rank augmentation of the RMV-form of spectral data using gas consumption data

Case 2 in Section 3.3.2 is considered to illustrate rank augmentation of the RMV-form of spectral data. Here, the chlorination of butanoic acid (BA) takes place in the organic solvent (Q) in the liquid phase. The total volume and the flowrate of the gaseous purge outlet are considered to be constant. The reaction system is kept isothermal by a heating-cooling system, and Assumptions (A5)-(A8) in Section 5.2 are valid. Table 5.8 indicates the ranks of the noise-free data matrices \mathbf{H}_{rm} and \mathbf{H}_{rm}^{aug} for Case 2 in Section 5.2.4, the number of absorbing species (denoted S) and p_a .

It is assumed that Q , BA, and Cl_2 absorb. Hence, the total number of absorbing reacting species is two, and the two reactions can be observed from the spectral matrix in RMV-form. Since two reactions and the mass transfer of Cl_2 cannot be observed from the two absorbing species, \mathbf{H}_{rm} is rank deficient with $\text{rank}(\mathbf{H}_{rm}) = S_r = 2 < R + p_{gl} = 3$. However, augmentation to full rank can be achieved by appending gas consumption data to \mathbf{H}_{rm} , thus leading to $\text{rank}(\mathbf{H}_{rm}^{aug}) = R + p_a = 3$ (see Column 5 in Table 5.8). Note that \mathbf{A} is of full rank S . However, only after appending the gas consumption data does the augmented matrix contain information on all R reactions and p_a mass transfers. Similarly, the gas consumption data can be used to augment the rank of \mathbf{H}_{rm} for the case when Q , MBA, and Cl_2 or Q , DBA, and Cl_2 absorb.

Table 5.8 Computed ranks of \mathbf{H}_{rm} and \mathbf{H}_{rm}^{aug} as functions of S , the number of absorbing species, and p_a , the number of species transferring between phases that do absorb. Rank deficiency is indicated by †. ($R_l = 2$, $p_{gl} = 1$, $p_{lg} = 1$).

S	p_a	Absorbing species	Rank of	
			\mathbf{H}_{rm}	\mathbf{H}_{rm}^{aug} (using $\mathbf{\Omega}_a$)
3	p_{gl}	{Q, BA, Cl ₂ } or {Q, MBA, Cl ₂ } or {Q, DBA, Cl ₂ }	2 [†]	3

5.6 Summary

Being able to compute the contributions of reactions and mass transfers from measured reaction data is key for investigating reaction systems. Concentration data from homogeneous and G–L reaction systems and spectral data from G–L reaction systems have been considered in this chapter. Various approaches to compute the extents of reaction and mass transfer from concentrations and spectral data with known pure-component spectra can also be proposed.

For homogeneous reaction systems, the linear transformation of Section 2.3 has been applied to compute the extents of reaction when the concentrations of all species are measured. When the concentrations of only a subset of species are measured, the flow-based approach of Section 4.2.2 using the inlet and outlet flowrates has been used to compute the extents of reaction. For the case of concentrations corrupted with zero-mean Gaussian noise, it has been shown that the computed extents of reaction are unbiased.

For G–L reaction systems, the linear transformation of Section 3.2.1 has been applied to compute the extents of reaction, mass transfer and flow from the concentration measurements of all species in the liquid phase. When the concentrations are measured only for subsets of the species in the gas and liquid phases, the flow-based approach of Section 4.3.2 has been applied to compute the extents of reaction and mass transfer by solving a set of differential-algebraic equations using the inlet and outlet flowrates and the liquid and gas masses. For the case of concentrations corrupted with zero-mean Gaussian noise, it has been shown that the computed extents of reaction and mass transfer are unbiased.

It has also been shown that the linear transformation of Section 3.2.1 can be extended to spectral data when the pure component spectra are known. When the pure-component spectra are unknown, a transformation to compute spectral data in RMV-form using the inlet and initial spectra and the inlet and outlet flowrates has been proposed. The resulting RMV-form contains only the contributions of the unknown reactions and mass transfers. Furthermore, it has been shown that spectral data in RMV-form are typically full rank and thus do not require rank augmentation for the application of FA methods. However, in case of rank deficiency of the transformed spectral data due to unobserved absorbing transferring species, a method for rank augmentation by appending gas consumption data to the spectral data has been proposed. Furthermore, a parameter estimation problem has been formulated that estimates simul-

taneously the parameters of reaction- and mass-transfer-rate expressions based on the RMV-form of spectral data. This method is called *simultaneous identification approach*.

Using the computed extents of reaction and mass transfer and the integral method, parameter estimation problems have been formulated to identify the parameters of each reaction-rate and each mass-transfer-rate expression individually. It has been shown that the incremental identification approach using the differential method can be adapted to the integral method using the approaches proposed in Sections 5.1 and 5.4. This leads to a novel incremental identification approach using the integral method. Furthermore, the main steps of various incremental identification approaches available in the literature and the one proposed in this chapter are summarized for homogeneous and G–L reaction systems. This summary can be seen as a starting point toward the comparison of various incremental identification approaches. The outlook of Chapter 6 discusses several issues to be investigated in future work based on the comparison in Section 5.4.3.

Chapter 6

Conclusions

6.1 Summary of main results

The concept of extents of reaction and mass transfer developed in this dissertation is a further step toward building reliable process models. The developed concepts help speed up process development and provide a better understanding of the reaction systems.

Extents of reaction, mass transfer and flow

The reaction variants and invariants in the literature for open homogeneous reaction systems are merely mathematical quantities devoid of any physical meaning. A way to improve interpretation was investigated in Chapter 2 for open homogeneous reaction systems. A linear transformation of the number of moles vector was proposed that enables to view the reaction variants as extents of reaction, the inlet-flow variants as extents of inlet flow, and the outlet-flow variant as extent of outlet flow. The linear transformation was developed using information about the stoichiometry, the inlet compositions and the initial conditions. Furthermore, the invariant states remain constant at zero, which allows dropping them from the transformed dynamic model, thereby leading to model-order reduction.

The developed linear transformation for open homogeneous reactors was extended to open G–L reaction systems in Chapter 3. The numbers of moles in the liquid and gas phases were transformed linearly into extents of reaction, extents of mass transfer, and extents of inlet and outlet flows. The extension to open G–L reaction systems has led to a novel concept of extent of mass transfer in the liquid and gas phases. Hence, a major contribution of this dissertation is the development of a *linear transformation* that decouples the effects of each reaction and each mass transfer and enables one to compute the extent of each reaction and each mass transfer from the numbers of moles.

Minimal state representation and state reconstruction

Minimal state representations of homogeneous and G–L reaction systems were studied in Chapter 4 using the transformed models. The conditions under which linearly

transformed models are minimal state representations were derived using the concept of accessibility of nonlinear systems. It has been shown that minimal state representations are of the order $(R + p + 1)$ for open homogeneous reactors and $(R + 2p_m + p_l + p_g + 2)$ for open G–L reactors. Furthermore, the reconstruction of unmeasured concentrations from the measured ones was studied using the proposed transformations in Chapter 4. Using measured flowrates, the transformations can be used to reconstruct unmeasured concentrations. Moreover, it has been shown that the minimal number of concentration measurements required to reconstruct unmeasured species is R for open homogeneous reactors and $(R + p_m)$ for open G–L reactors.

Use of concentrations and spectral data

Obtaining reliable descriptions of kinetics and transport phenomena is a challenging task in the modeling of chemical reaction systems. In practice, the description of these phenomena is obtained through the analysis of measured concentrations and spectral data. The linear transformations developed in Chapters 2 and 3, and the methods developed in Chapter 4 were used for the analysis of measured data in Chapter 5. For measured concentrations, and spectral data with knowledge of the pure-component spectra, the linear transformation has been applied to compute the extents of reaction and mass transfer. The methods developed in Chapter 4 have been applied to compute extents for the special case where concentrations are only available for a subset of the reacting species. Moreover, the computed extents of reaction and mass transfer have been used to identify the unknown reaction and mass-transfer rates individually using the integral method. The error propagation in the computation of extents has been treated for the case of concentrations corrupted with zero-mean Gaussian noise. It has been shown that the extents computed by the approaches proposed in Chapter 5 give unbiased estimates of extents. Furthermore, it has been shown that the incremental identification approach using the differential method can be adapted to the integral method. This leads to a novel incremental identification approach using the integral method.

The case of spectral data with unknown pure-component spectra was briefly treated in Chapter 5. Using the measured inlet and initial spectra, RMV-form of spectral data has been computed from the raw spectral data. The RMV-form is typically of full rank and, hence, the factor-analytical methods in the literature can be applied. However, it was shown that the gas consumption data can be used to augment the rank of spectral data in the RMV-form, if RMV-form of spectral data matrix is rank deficient. An approach to identify each reaction and mass-transfer rate parameters simultaneously from spectral data in RMV-form has been formulated.

To put the present work in perspective, the simultaneous and incremental identification approaches in the literature and the incremental identification approach proposed in this work are compared schematically in Figure 6.1.

Path "1" indicates the simultaneous identification approach using the integral method, whereby rate expressions for all the reactions are integrated to simulate the concentrations that are fitted to the measured ones via a least-squares problem.

Path "2" represents the incremental identification approach using the differential method, whereby the rate of the i th reaction is computed by differentiation of the concentration measurements and use of information regarding the stoichiometry, the inlet composition, the volume, and the inlet and outlet flowrates. The i th rate model, which is chosen from the database of rate expressions, is fitted to the computed rate via a least-squares problem.

Path "3" represents the incremental identification approach using the integral method proposed in this thesis, whereby the extent of i th reaction is computed using the linear transformation from the concentration measurements and information regarding the stoichiometry, the inlet composition, the volume, and the initial conditions. The i th rate model, which is chosen from the database of rate expressions, is identified from the corresponding computed extent via a least-squares problem using the integral method. The proposed incremental identification approach using integral method combines the strengths of the incremental approach (can handle each reaction individually) and the integral method (optimal handling of the noise).

Table 6.1 summarizes the problems addressed in this dissertation, the tools proposed or used to solve them, and the corresponding implications.

Experiments, measurements
and required information

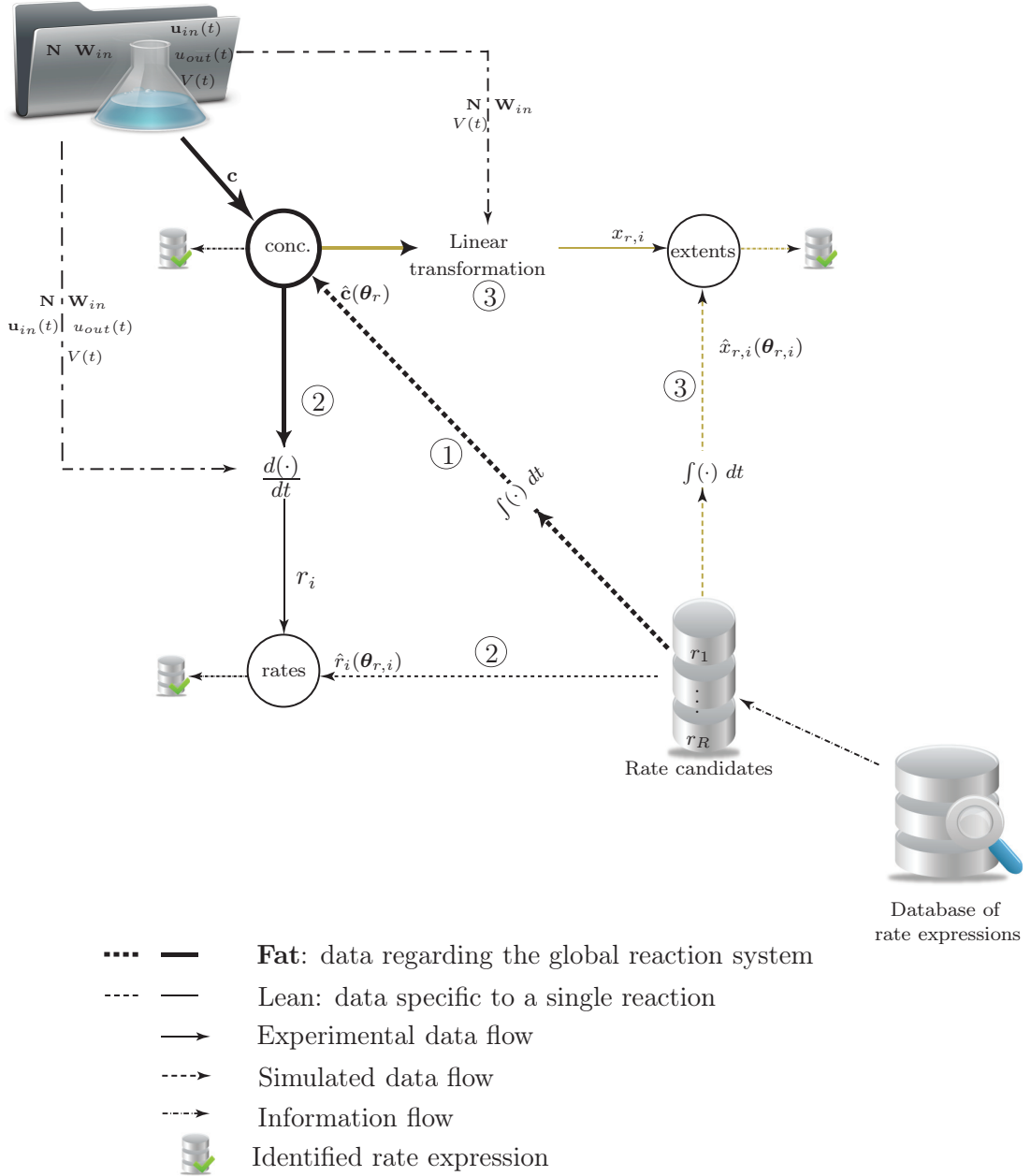


Figure 6.1 Schematic comparison of the simultaneous and incremental identification approaches of homogeneous reaction systems. Path 1, simultaneous approach that uses the integral method to integrate the candidate of all rate expressions; Path 2, incremental approach that uses the differential method to differentiate concentrations; Path 3, *incremental approach proposed in this thesis* that uses the integral method to integrate a single rate expression at the time.

Table 6.1 An overview of the problems addressed in this dissertation, the tools proposed to solve them, and the corresponding implications.

Problems	Tools developed/studied	Implications
P1. Building of first-principles models	Linear transformation	Can compute the extents of reaction and mass transfer from concentrations and spectral data without knowledge of reaction and mass-transfer rates.
	State reconstruction	Can predict the unmeasured concentrations without knowledge of reaction and mass-transfer rates from the available measurements.
	Integral method	Can estimate the parameters of individual reaction and mass-transfer rates from the computed extents of reaction and mass transfer from concentrations and spectral data.
P2. Simplification of dynamic models	Linear transformation	Can transform coupled dynamic models to physical meaningful states and remove redundant elements.
P3. Monitoring, control and optimization	Minimal state representation	Can help build first-principles model
		Can determine the minimal model of reaction systems.
		Can determine the minimal number of species needed to be measured for the reconstruction of unmeasured concentrations.

6.2 Outlook

The concept of extents of reaction, mass transfer, and flow was developed in Chapters 2 and 3 through analysis of dynamic reaction models. The uses of extents for minimal state representation, state reconstruction and the identification of a kinetic model based on concentrations and spectral data were investigated in the previous chapters. However, there are still important questions that could be addressed in future work. This section presents some follow-up questions and implications of the developed concepts, regarding the identification of a kinetic model from measured reaction data and model reduction.

6.2.1 Comparison of various incremental identification approaches

Several issues concerning extent- and rate-based methods presented in Section 5.4.3 could be distinguished as follows:

1. **Numerical differentiation vs. integration of data:** The rate-based methods are related to the *differential method* and require time differentiation of noisy data, which is a difficult task that calls for appropriate regularization [100]. The extent-based methods, which are related to the *integral method*, require integration that involves both low- and high-resolution data.

In practice, concentrations are typically measured only infrequently, whereas the flowrates and volume are available almost continuously. This leads to low-resolution concentration data, $\mathbf{c}(t_h)$, and high-resolution flowrate and volume data, $\mathbf{u}_{in}(t)$, $u_{out}(t)$ and $V(t)$, respectively. Methods O1, R2, P1 and P2 in Tables 5.2, and 5.3 require integration of low-resolution data and are thus of limited accuracy, whereas method V2 calls for the integration of high-resolution data.

Continuous approximation of discrete low-resolution measurements is often required for the differentiation in methods R1, R2 and R3¹ and for the integration in methods O1, R2, P1 and P2. This continuous approximation involves additional meta-parameters. For example, $\tilde{\mathbf{c}}(t) = \sum_{h=0}^H \mathbf{c}(t_h)\phi_h(t)$, where $\tilde{\mathbf{c}}(t)$ represents a continuous function approximation of the concentrations based on the low-resolution data $\mathbf{c}(t_h)$ and the basis functions $\phi_h(t)$, $h = 0, \dots, H$.

Hence, a detailed investigation of the relative merits and drawbacks of numerical integration and differentiation of measured reaction data in the identification of kinetics would be interesting in the further development of these methods.

2. **Error propagation:** In the presence of only a limited number of noisy concentration measurements, the integral method typically has statistical advantage over the differential method. Nowadays, concentrations can be estimated frequently from on-line spectral data using multivariate calibration (MVC) or multivariate curve resolution

¹ Depending on the numerical method, differentiation may not require a function representation of low-resolution data.

(MCR). However, both concentration measurements and estimates contain errors due to measurement noise or modeling errors in MVC and MCR.

Methods V1 and V2 give unbiased estimates of extents while methods R1, R2 and R3 give biased estimates of rates. For method O1, the error propagation from concentrations to the estimated extents needs to be investigated. A study of the effect of error propagation from the estimated extents and rates the estimated rate parameters should be investigated in detail similar to that was done in [10, 13].

3. **Model discrimination:** Methods P1 and P2 involve a regression problem with a dynamic model, while the method P3 involves a regression problem with a static model. The discrimination power of the extent- and rate-based methods based on a proper metric and computational efficiency, when two or more competing kinetic structures are proposed, should be investigated.
4. **Experimental data:** In this dissertation, simulated examples have been presented to illustrate the identification of kinetic models. These methods should be applied to experimental data, using also spectral measurements.

6.2.2 Use of spectral, calorimetric and gas consumption data

Computation of extents of reaction and mass transfer

In Chapter 5, an approach to estimate kinetic parameters from spectral data in RMV-form was presented. This approach assumes that the structures of reaction and mass-transfer rates are known. However, these structures are rarely known in practice. FA methods (e.g. multivariate curve resolution) can be applied to spectral data to estimate the unknown concentration profiles and the pure-component spectra. The estimated concentrations can be used for incremental identification as described in the previous section. However, FA methods cannot be applied to rank-deficient spectral data. In contrast to spectral data, the RMV-form of spectral data is typically of full rank. Hence, a constrained optimization approach based on FA methods to compute the extents of reaction and mass transfer from the RMV-form of spectral data would be interesting to investigate, with emphasis on the following two aspects:

- **Constraints formulation:** Importance is given to the formulation of appropriate constraints such as the kinetic model, the available initial and final concentration measurements [2], the pure-component spectra of a subset of species, non-negativity, continuous increasing or decreasing (monotonous) profiles of extents, unimodality. Additional measurements such as calorimetric data and the compositions measured in an exhaust gas can also be formulated as constraints.
- **Drift-correction:** The pure-component spectra of a subset of species can often be measured independently of the reaction runs. However, these pure-component spectra change in the reacting mixture. It is proposed to use drift-correction methods to compensate for these drifts [39].

6.2.3 Model reduction

The model order can also be reduced by eliminating the fast modes using, for example, singular perturbation theory [34, 94]. Since the reactions (and not the numbers of moles) exhibit fast and slow dynamics behavior, the numbers of moles typically cannot be classified as fast or slow states. Hence, the mole balances in Eq. (2.1) for homogeneous reactors and Eqs. (3.9) and (3.10) for G–L reactors are less suited for application of singular perturbation. In contrast, the extents of reaction \mathbf{x}_r and the extents of mass transfer $\mathbf{x}_{m,f}$, $f = \{g, l\}$ are direct functions of the reaction rates and the mass-transfer rate, and thus can be separated into fast and slow dynamics.

For homogeneous reaction systems, the extents of reaction can be transformed into a form suited to singular perturbation theory. The rate of the i th reaction can be expressed as the product of a rate constant k_i and a nonlinear function $\bar{\mathbf{r}}_i(\mathbf{n})$. Let us assume that there are R_s slow reactions and $(R - R_s)$ fast reactions. The reactions are ordered according to their relative speed, that is $i = 1, \dots, R_s$ for the slow reactions and $i = R_s + 1, \dots, R$ for the fast reactions. It is also assumed that $\frac{k_{R_s+1}}{k_i} \gg O(1)$ for $i = 1, \dots, R_s$ and $\frac{k_{R_s+1}}{k_i} \cong O(1)$ for $i = R_s + 1, \dots, R$, where $O(1)$ indicates the order of magnitude of one. With this formulation the extents of reaction vector \mathbf{x}_r can be written as follows: $\mathbf{x}_r = \begin{bmatrix} \mathbf{x}_r^s \\ \mathbf{x}_r^f \end{bmatrix}$, where \mathbf{x}_r^s and \mathbf{x}_r^f are the R_s - and $(R - R_s)$ -dimensional vectors corresponding to the R_s slow and $(R - R_s)$ fast reactions, respectively. The dynamics of \mathbf{x}_r^s and \mathbf{x}_r^f can be written in terms of the corresponding reaction rates as follows:

$$\begin{aligned}\dot{\mathbf{x}}_r^s &= V\mathbf{r}^s - \frac{u_{out}}{m}\mathbf{x}_r^s, \\ \dot{\mathbf{x}}_r^f &= V\mathbf{r}^f - \frac{u_{out}}{m}\mathbf{x}_r^f.\end{aligned}\tag{6.1}$$

The fast reaction rates \mathbf{r}^f can be expressed as follows:

$$\mathbf{r}^f = \mathbf{K}\bar{\mathbf{r}}^f,\tag{6.2}$$

$$= k_{R_s+1}\bar{\mathbf{K}}\bar{\mathbf{r}}^f,\tag{6.3}$$

where $\bar{\mathbf{K}} = \text{diag}\left([1, \frac{k_{R_s+2}}{k_{R_s+1}}, \dots, \frac{k_R}{k_{R_s+1}}]\right)$ the $(R - R_s)$ -dimensional diagonal matrix and $\bar{\mathbf{r}}^f$ is the $(R - R_s)$ -dimensional vector of nonlinear functions. With \mathbf{r}^f and defining $\epsilon = 1/k_{R_s+1}$, Eq. (6.1) can be formulated as follows:

$$\begin{aligned}\dot{\mathbf{x}}_r^s &= V\mathbf{r}^s - \frac{u_{out}}{m}\mathbf{x}_r^s, \\ \epsilon \dot{\mathbf{x}}_r^f &= V\bar{\mathbf{K}}\bar{\mathbf{r}}^f - \frac{u_{out}}{m}\epsilon \mathbf{x}_r^f,\end{aligned}\tag{6.4}$$

Eq. (6.4) corresponds to the standard singular perturbation model [46]. Hence, the extents of reaction and mass transfer are well suited to the singular perturbation theory

and it would be interesting to investigate the utility of the extents of reaction and mass transfer for further order-reduction through singular perturbation.

6.2.4 Other implications

Parametric sensitivity analysis:

Parametric sensitivity analysis is simplified by working with the extents of reaction instead of the numbers of moles, since the 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 and mass transfer is the fact that they are orthogonal to the inlet space, thereby leading to $\partial \mathbf{x}_r / \partial \mathbf{u}_{in} = \mathbf{0}_{R \times p}$ and $\partial \mathbf{x}_{m,t} / \partial \mathbf{u}_{in} = \mathbf{0}_{p_m \times p}$.

Attainable-region approach:

Determining the optimal reaction network is the main objective in reactor synthesis problems. The basic question regards the amount of material that can be produced from all possible steady-state reactor configurations. The set of all possible concentrations that can be achieved with any of the available reactor configurations under given constraints is called the *attainable region* [29, 36, 37]. For a set of reactors at steady state, Omtveit et al. [61] proposed a method to construct the attainable region in the concentration space of a few linearly independent species using the concept of reaction invariants. It may be convenient to work with the lower-dimensional space of the extents of reaction and flow to construct the attainable region and examine the various reactor configurations.

Appendix A

Proofs

A.1 Proof of Theorem 2.1

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 $[\mathbf{N}^T \ \mathbf{L} \ \mathbf{Q}]$ is of rank S ,
- C2: The columns of \mathbf{Q} are orthonormal and span the null space of $[\mathbf{N}^T \ \mathbf{W}_{in}]^T$,
- C3: The columns of \mathbf{L} are orthonormal and span the null space of $[\mathbf{N}^T \ \mathbf{Q}]^T$,
- C4: $\mathbf{M}^T \mathbf{W}_{in} = \mathbf{I}_p$, which can be achieved by choosing $\mathbf{M} = \mathbf{L}(\mathbf{W}_{in}^T \mathbf{L})^+$.

With $\mathbf{S}^T = \mathbf{N}^{T+}(\mathbf{I}_S - \mathbf{W}_{in} \mathbf{M}^T)$, the conditions C1–C4 enforce the conditions shown under the braces in Eq. (2.12). Applying the transformation (2.13) to Eq. (2.1) gives:

$$\begin{aligned} \dot{\mathbf{z}}_r &= V\mathbf{r} - \frac{u_{out}}{m} \mathbf{z}_r, & \mathbf{z}_r(0) &= \mathbf{S}^T \mathbf{n}_0, \\ \dot{\mathbf{z}}_{in} &= \mathbf{u}_{in} - \frac{u_{out}}{m} \mathbf{z}_{in}, & \mathbf{z}_{in}(0) &= \mathbf{M}^T \mathbf{n}_0, \\ \dot{\mathbf{z}}_{iv} &= -\frac{u_{out}}{m} \mathbf{z}_{iv}, & \mathbf{z}_{iv}(0) &= \mathbf{Q}^T \mathbf{n}_0. \end{aligned} \tag{A.1}$$

Next, Eq. (2.15) needs to be proven. For this, the following properties resulting from Conditions C1–C4 are used:

$$\begin{aligned} \mathbf{N}^T \mathbf{N}^{T+} + \mathbf{L} \mathbf{L}^T + \mathbf{Q} \mathbf{Q}^T &= \mathbf{I}_S && \text{(complementary orthonormal spaces),} \\ \mathbf{Q} \mathbf{Q}^T \mathbf{W}_{in} \mathbf{M}^T &= \mathbf{0}_{S \times S} && \text{(inlet space rotated orthogonally to } \mathbf{Q} \mathbf{Q}^T \text{ by construction of} \\ & && \mathbf{M} = \mathbf{L}(\mathbf{W}_{in}^T \mathbf{L})^+, \\ \mathbf{L} \mathbf{L}^T \mathbf{W}_{in} \mathbf{M}^T &= \mathbf{L} \mathbf{L}^T && \text{(equivalent spaces).} \end{aligned} \tag{A.2}$$

Pre-multiplying both sides of Eq. (2.13) with $[\mathbf{N}^T \ \mathbf{W}_{in} \ \mathbf{Q}]$ gives:

$$\begin{aligned}
\mathbf{N}^T \mathbf{z}_r + \mathbf{W}_{in} \mathbf{z}_{in} + \mathbf{Q} \mathbf{z}_{iv} &= (\mathbf{N}^T \mathbf{S}^T + \mathbf{W}_{in} \mathbf{M}^T + \mathbf{Q} \mathbf{Q}^T) \mathbf{n} \\
&= (\mathbf{N}^T \mathbf{N}^{T+} (\mathbf{I}_S - \mathbf{W}_{in} \mathbf{M}^T) + \mathbf{W}_{in} \mathbf{M}^T + \mathbf{Q} \mathbf{Q}^T) \mathbf{n} \\
&= (\mathbf{N}^T \mathbf{N}^{T+} + (\mathbf{L} \mathbf{L}^T + \mathbf{Q} \mathbf{Q}^T) \mathbf{W}_{in} \mathbf{M}^T + \mathbf{Q} \mathbf{Q}^T) \mathbf{n} \quad (\text{A.3}) \\
&= (\mathbf{N}^T \mathbf{N}^{T+} + \mathbf{L} \mathbf{L}^T + \mathbf{Q} \mathbf{Q}^T) \mathbf{n} = \mathbf{n} \\
\iff \mathbf{n} &= \mathbf{N}^T \mathbf{z}_r + \mathbf{W}_{in} \mathbf{z}_{in} + \mathbf{Q} \mathbf{z}_{iv}.
\end{aligned}$$

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

A.2 Proof of Theorem 2.2

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

In the second part of the proof, Eqs. (2.20) and (2.23) are derived. For this, the following properties resulting from Conditions C1–C4 are used: $\mathbf{q}_0^T \mathbf{N}^T = \mathbf{0}_R^T$, $\mathbf{q}_0^T \mathbf{W}_{in} = \mathbf{0}_p^T$, and $\mathbf{q}_0^T \mathbf{n}_0 = 1$. Applying the transformation (2.18) and

$$\mathbf{x}_{iv} = \mathbf{Q}_0^T \mathbf{n} \quad \text{with} \quad \mathbf{Q}_0^T = \mathbf{Q}^T (\mathbf{I}_S - \mathbf{n}_0 \mathbf{q}_0^T) \quad (\text{A.4})$$

to Eq. (2.1) gives:

$$\begin{aligned}
\dot{\mathbf{x}}_r &= V \mathbf{r} - \frac{u_{out}}{m} \mathbf{x}_r, & \mathbf{x}_r(0) &= \mathbf{0}_R, \\
\dot{\mathbf{x}}_{in} &= \mathbf{u}_{in} - \frac{u_{out}}{m} \mathbf{x}_{in}, & \mathbf{x}_{in}(0) &= \mathbf{0}_p, \\
\dot{\lambda} &= -\frac{u_{out}}{m} \lambda, & \lambda(0) &= 1, \\
\dot{\mathbf{x}}_{iv} &= -\frac{u_{out}}{m} \mathbf{x}_{iv}, & \mathbf{x}_{iv}(0) &= \mathbf{0}_{S-R-p}.
\end{aligned} \quad (\text{A.5})$$

Since $\mathbf{x}_{iv}(0) = \mathbf{0}_{S-R-p}$, $\mathbf{x}_{iv}(t) = \mathbf{0}_{S-R-p}$ for all time t . Hence, \mathbf{x}_{iv} can be dropped from Eq. (A.5).

In the last part of the proof, Eq. (2.21) is derived. For this, the following properties are used: (i) Eq. (A.2), (ii) $\mathbf{Q} \mathbf{x}_{iv}(t) = \mathbf{0}_S$ since $\mathbf{x}_{iv}(t) = \mathbf{0}_{S-R-p}$, and (iii) $(\mathbf{N}^T \mathbf{S}^T + \mathbf{W}_{in} \mathbf{M}^T + \mathbf{Q} \mathbf{Q}^T) = \mathbf{I}_S$ from Eq. (A.3). Pre-multiplying both sides of Eq. (2.18) with $[\mathbf{N}^T \ \mathbf{W}_{in} \ \mathbf{n}_0]$ leads to:

$$\begin{aligned}
\mathbf{N}^T \mathbf{x}_r + \mathbf{W}_{in} \mathbf{x}_{in} + \lambda \mathbf{n}_0 &= \mathbf{N}^T \mathbf{x}_r + \mathbf{W}_{in} \mathbf{x}_{in} + \lambda \mathbf{n}_0 + \mathbf{Q} \mathbf{x}_{iv} \\
&= (\mathbf{N}^T \mathbf{S}^T + \mathbf{W}_{in} \mathbf{M}^T + \mathbf{Q} \mathbf{Q}^T) (\mathbf{I}_S - \mathbf{n}_0 \mathbf{q}_0^T) \mathbf{n} + \mathbf{n}_0 \mathbf{q}_0^T \mathbf{n} \quad (\text{A.6}) \\
&= (\mathbf{I}_S - \mathbf{n}_0 \mathbf{q}_0^T) \mathbf{n} + \mathbf{n}_0 \mathbf{q}_0^T \mathbf{n} = \mathbf{n} \\
\iff \mathbf{n}(t) &= \mathbf{N}^T \mathbf{x}_r(t) + \mathbf{W}_{in} \mathbf{x}_{in}(t) + \mathbf{n}_0 \lambda(t).
\end{aligned}$$

A.3 Proof of Lemma 4.2

The proof of Lemma 4.2 follows by contradiction. Let assume that there exists a transformation $\Phi: \xi_1 \rightarrow [\mathbf{y}_1]$ independent of for all inputs $u_i, i = 1, \dots, v$ such that the dynamics of the system (4.6) can further be reduced as follows:

$$\begin{aligned} \dot{\mathbf{y}}_1 &= \tilde{\mathbf{f}}(\mathbf{y}(t)) + \sum_{i=1}^k \tilde{\mathbf{g}}_i(\mathbf{y})u_i \\ \dot{\mathbf{y}}_2 &= \mathbf{0} \end{aligned} \tag{A.7}$$

In Eq. (A.7), since \mathbf{y}_2 states are constant and hence are not affected by the inputs $u_i, \forall i = 1, \dots, v$, the states \mathbf{y}_2 are inaccessible states. However, the system (4.6) is locally accessible by assumption. Hence, there does not exist a transformation Φ that leads to decomposition of ξ_1 states into accessible states \mathbf{y}_1 and inaccessible states \mathbf{y}_2 . Thus, the dimension of states in ξ cannot further be reduced.

A.4 Proof of Lemma 4.3

The proof of Lemma 4.3 follows by construction. Let consider the accessibility distribution in Eq. (4.5) with $k = 1$:

$$\begin{aligned} \Delta_1 &= \begin{bmatrix} \mathbf{G} & [\mathbf{f}, \mathbf{G}] \end{bmatrix} \\ &= \begin{bmatrix} \mathbf{0}_{R \times p} & -\frac{\mathbf{x}_r}{m} & -\mathbf{J}(t) \\ \mathbf{I}_p & -\frac{\mathbf{x}_{im}}{m} & \mathbf{0}_{p \times v+1} \\ \mathbf{0}_{1 \times p} & -\frac{\lambda}{m} & \mathbf{0}_{1 \times v+1} \end{bmatrix}. \end{aligned} \tag{A.8}$$

Since $\lambda \neq 0$ and the rank of $\mathbf{J} = R$ by assumption, $\dim(\Delta_1) = (R + v)$. Hence, the result of Lemma 4.1 proves that the system is locally accessible.

A.5 Proof of Theorem 4.1

The idea of the proof is to show that Eq. (4.6) does not contain redundant states. Since the rank of $\mathbf{J}(t) = R$ by assumption, the distribution Δ_1 has full rank $(R + v)$. Hence, the reaction system in Eq. (4.6) is accessible as proved in Lemma 4.3. As a consequence of Lemma 4.2 and the accessibility of the reaction system in Eq. (4.6), the dimension of Eq. (4.6) cannot be reduced and thus Eq. (4.6) does not contain redundant states. This proves Theorem 4.1.

A.6 Proof of Theorem 4.2

The numbers of moles vector can be partitioned into the available and unavailable numbers of moles as follows:

$$\mathbf{n}(t) = \begin{bmatrix} \mathbf{n}_a(t) \\ \mathbf{n}_u(t) \end{bmatrix} = \begin{bmatrix} \mathbf{N}_a^T \\ \mathbf{N}_u^T \end{bmatrix} \mathbf{x}_r(t) + \begin{bmatrix} \mathbf{W}_{in,a} \\ \mathbf{W}_{in,u} \end{bmatrix} \mathbf{x}_{in}(t) + \begin{bmatrix} \mathbf{n}_{0,a} \\ \mathbf{n}_{0,u} \end{bmatrix} \lambda(t) \quad (\text{A.9})$$

Since \mathbf{u}_{in} and u_{out} are available, the states $\mathbf{x}_{in}(t)$ and $\lambda(t)$ can be computed from Eqs. 4.8 and 4.9, respectively. Since it is assumed that the number of available measurements $S_a \geq R$ and $\text{rank}(\mathbf{N}_a) = R$, $(\mathbf{N}_a^T)^+$ exists. Hence the unknown part in Eq. (A.9), the extents of reaction \mathbf{x}_r , can be computed from the available numbers of moles and the computed $\mathbf{x}_{in}(t)$ and $\lambda(t)$ from the Eq. 4.10. In addition to \mathbf{N}_u and $\mathbf{W}_{in,u}$, the initial conditions of unmeasured species, $\mathbf{n}_{0,u}$ are also available. Hence, using Eq. (4.11), $\mathbf{n}_u(t)$ can be reconstructed from computed quantities as in Eq. (A.9).

A.7 Proof of Theorem 4.3

By defining $\mathbf{y}_1 = \mathbf{x}_{m,l}$, $\mathbf{y}_2 = \mathbf{x}_{m,g}$, $y_3 = \lambda_l$, $y_4 = \lambda_g$ and $\mathbf{u}_1 = \boldsymbol{\zeta}$, $u_2 = -u_{out,l}/m_l$, $u_3 = -u_{out,g}/m_g$, Eq. (4.12) becomes:

$$\dot{\mathbf{y}} = \mathbf{g}_1 \mathbf{u}_1 + \mathbf{g}_2 u_2 + \mathbf{g}_3 u_3 + \mathbf{g}_4 u_4, \quad (\text{A.10})$$

where

$$\mathbf{g}_1 = \begin{bmatrix} \mathbf{I}_{p_m \times p_m} \\ 0 \\ \mathbf{I}_{p_m \times p_m} \\ 0 \end{bmatrix}, \mathbf{g}_2 = \begin{bmatrix} -\mathbf{y}_1 \\ -y_3 \\ \mathbf{0}_{p_m} \\ 0 \end{bmatrix}, \mathbf{g}_3 = \begin{bmatrix} \mathbf{0}_{p_m} \\ 0 \\ \mathbf{y}_2 \\ -y_4 \end{bmatrix} \quad (\text{A.11})$$

If the set of $(2p_m + 2)$ states in Eq. (A.10) is accessible in finite time, then it can be inferred that there are no redundant elements according to Lemma 4.2. Let $\bar{\Delta}$ be a distribution of Eq. (A.10). Then, the rank of $\bar{\Delta}$ must be $2p_m + 2$:

$$\dim \bar{\Delta} = \text{span}\{\mathbf{g}_1, \mathbf{g}_2, \dots, [\mathbf{g}_1, \mathbf{g}_2], [\mathbf{g}_1, \mathbf{g}_3], \dots\} = 2p_m + 2, \quad (\text{A.12})$$

where $[\mathbf{g}_1, \mathbf{g}_2]$ is the Lie-bracket of \mathbf{g}_1 and \mathbf{g}_2 . It can easily be shown that $\bar{\Delta}$ has full rank already with $[\mathbf{g}_2, \mathbf{g}_3]$:

$$\bar{\Delta} = \begin{bmatrix} \mathbf{I}_{p_m \times p_m} & -\mathbf{y}_1 & \mathbf{0}_{p_m} & \mathbf{I}_{p_m \times p_m} & \mathbf{0}_{p_m \times p_m} \\ \mathbf{0}_{1 \times p_m} & -y_3 & 0 & \mathbf{0}_{1 \times p_m} & \mathbf{0}_{1 \times p_m} \\ \mathbf{I}_{p_m \times p_m} & \mathbf{0}_{p_m} & -\mathbf{y}_2 & \mathbf{0}_{p_m \times p_m} & \mathbf{I}_{p_m \times p_m} \\ \mathbf{0}_{1 \times p_m} & 0 & -y_4 & \mathbf{0}_{1 \times p_m} & \mathbf{0}_{1 \times p_m} \end{bmatrix} \quad (\text{A.13})$$

since $y_3 \neq 0$ and $y_4 \neq 0$, the rank $(\bar{\Delta}) = 2p_m + 2$. Hence, the subsystem in Eq. (4.12) is accessible and hence, the G-L reaction system with outlet cannot further be reduced by any transformation.

A.8 Proof of Proposition 4.5

The $S_{g,a}$ algebraic equations can be written through the measured numbers of moles in the gas phase as in Eq. (4.19). $\mathbf{u}_{in,g}(t)$ and $u_{out,g}(t)$ are available, hence, $(p_g + 1)$ differential equations can be written for $\mathbf{x}_{in,g}$, and λ_g as in Eq. (4.21).

The $S_{l,a}$ algebraic equations can be written through measured numbers of moles in the liquid phase $\mathbf{n}_{l,a}$, as in Eq. (4.15). $\mathbf{u}_{in,l}(t)$ and $u_{out,l}(t)$ are available, hence, $(p_l + 1)$ differential equations can be written for $\mathbf{x}_{in,l}$, and λ_l , as in Eq. (4.17).

The liquid and gas masses m_l and m_g can be expressed in terms of the extents of mass transfer and inlet flow, and the discounting variables, as in Eqs. (4.16) and (4.20). It will lead to two algebraic equations. The relationship between $\mathbf{x}_{m,g}$, $\mathbf{x}_{m,l}$ and δ_m will lead to p_m differential equations in Eq. (4.22) and p_m algebraic equations in Eq. (4.23).

Hence, there are total $(S_{g,a} + S_{l,a} + p_m + 2)$ algebraic equations and there are $(p_l + p_g + p_m + 2)$ differential equations. Since rank $(\mathbf{W}_{m,g,g,a}) = p_{m_g}$ by Assumption (ii), its inverse exists. Hence, there are at least p_{m_g} independent algebraic equations out of $S_{g,a}$ equations in the gas phase. Similarly, by Assumption (iii) rank $([\mathbf{N}_a^T, \mathbf{W}_{m,l,l,a}]) \geq R + p_{m_l}$. Thus there are at least $(R + p_{m_l})$ independent algebraic equations out of $S_{l,a}$ equations in the liquid phase. By assumption of the independent inlets and mass-transfer, the $(p_l + p_g + p_m + 2)$ differential equations are also independent. This leads $(R + p_{m_g} + p_{m_l} + p_l + p_g + 2p_m + 4)$ independent differential-algebraic equations for the computation of the $(R + p_g + p_l + 3p_m + 4)$ unknown variables. Hence, one needs to satisfy $p_{g_a} + p_{l_a} \geq p_m$. Since this condition satisfies by the construction, the number of independent differential-algebraic equations is equal to the number of unknown variables. Hence, the formulated differential-algebraic equations in (4.15)-(4.23) can be solved to compute the unknown variables. This proves the theorem.

A.9 Proof of Proposition 5.1

The numbers of moles for the available species in the gas phase $\mathbf{n}_{g,a}$ can be computed from $\mathbf{c}_{g,a}$ as follows: $\mathbf{n}_{g,a}(t_h) = (V_t - V_l(t_h))\mathbf{c}_{g,a}(t_h)$. The available numbers of moles can be written in terms of various extents as follows:

$$\mathbf{n}_{g,a}(t) = -\mathbf{W}_{m,g,a} \mathbf{x}_{m,g}(t) + \mathbf{W}_{in,g,a} \mathbf{x}_{in,g}(t) + \mathbf{n}_{g0,a} \lambda_g(t). \quad (\text{A.14})$$

Since $\mathbf{u}_{in,g}(t)$, $u_{out,g}(t)$ and $m_g(t)$ are available, $\mathbf{x}_{in,g}(t)$ and $\lambda_g(t)$ can be computed from Eqs. (5.9a) and (5.9c). Since it is assumed that $S_{g,a} = p_{m_g}$ species measured in the gas phase are involved in mass transfer, $\mathbf{W}_{m,g,a}$ can be partitioned as follows: $\mathbf{W}_{m,g,a} = [\mathbf{W}_{m,g,g,a} \mathbf{0}_{p_{m_g} \times (p_m - p_{m_g})}]$. Then, Eq. (A.14) can be written as:

$$\mathbf{n}_{g,a}(t) = -\mathbf{W}_{m_g,g,a} \mathbf{x}_{m_g,g}(t) + \mathbf{W}_{in,g,a} \mathbf{x}_{in,g}(t) + \mathbf{n}_{l0,a} \lambda_g(t). \quad (\text{A.15})$$

By rearranging the terms, Eq. (5.9c) can be obtained. Since $\text{rank}(\mathbf{W}_{m_g,g,a}) = p_{m_g}$, its inverse exists. Thus, the extents of p_{m_g} mass transfer in the gas phase $\mathbf{x}_{m_g,g}(t)$ can be computed from Eq. (5.9c) by inverting $\mathbf{W}_{m_g,g,a}$.

Since $\mathbf{u}_{in,l}(t)$, $u_{out,l}(t)$ and $m_l(t)$ are also measured in addition to the gas flowrates, the extents of p_{m_g} mass transfer in the liquid phase $\mathbf{x}_{m_g,l}(t)$ can be computed from Eqs. 5.10a and 5.10b.

The numbers of moles for the available species in the liquid phase $\mathbf{n}_{l,a}$ can be computed from $\mathbf{c}_{l,a}$ as follows: $\mathbf{n}_{l,a}(t_h) = V_l(t_h)\mathbf{c}_{l,a}(t_h)$. The available numbers of moles in the liquid phase can be written in terms of various extents as follows:

$$\mathbf{n}_{l,a}(t_h) = \mathbf{N}_a^T \mathbf{x}_r(t_h) + \mathbf{W}_{m,l,a} \mathbf{x}_{m,l}(t_h) + \mathbf{W}_{in,l,a} \mathbf{x}_{in,l}(t_h) + \mathbf{n}_{l0,a} \lambda_l(t_h) \quad (\text{A.16})$$

$$\begin{aligned} &= \mathbf{N}_a^T \mathbf{x}_r(t_h) + [\mathbf{W}_{m_l,l,a} \mathbf{W}_{m_g,l,a}] \begin{bmatrix} \mathbf{x}_{m_l,l}(t_h) \\ \mathbf{x}_{m_g,l}(t_h) \end{bmatrix} + \mathbf{W}_{in,l,a} \mathbf{x}_{in,l}(t_h) \\ &\quad + \mathbf{n}_{l0,a} \lambda_l(t_h) \end{aligned} \quad (\text{A.17})$$

$$\begin{aligned} &= \mathbf{N}_a^T \mathbf{x}_r(t_h) + \mathbf{W}_{m_l,l,a} \mathbf{x}_{m_l,l}(t_h) + \mathbf{W}_{m_g,l,a} \mathbf{x}_{m_g,l}(t_h) + \mathbf{W}_{in,l,a} \mathbf{x}_{in,l}(t_h) \\ &\quad + \mathbf{n}_{l0,a} \lambda_l(t_h) \end{aligned} \quad (\text{A.18})$$

By rearranging Eq. (A.18), Eq. (5.11c) can be obtained. Since $\mathbf{u}_{in,l}(t)$, $u_{out,l}(t)$ and $m_l(t)$ are available, $\mathbf{x}_{in,l}(t_h)$ and $\lambda_l(t_h)$ can be computed from Eqs. (5.11a) and (5.11b). Since $S_{l,a} \geq R + p_m - p_{m_g}$ and $\text{rank}([\mathbf{N}_a^T, \mathbf{W}_{m_l,l,a}]) = R + p_{m_l}$ by assumption, the pseudo inverse of matrix $[\mathbf{N}_a^T, \mathbf{W}_{m_l,l,a}]$ exists and hence, the extents of reaction $\mathbf{x}_r(t)$ and $\mathbf{x}_{m_l,l}$ can be computed from Eq. (5.11c) by inverting the matrix $[\mathbf{N}_a^T, \mathbf{W}_{m_l,l,a}]$. This proves the theorem.

A.10 Proof of Corollary 5.5

Eq. (5.30) factorizes the volume-weighted spectral matrix \mathbf{A}_v to the matrices \mathcal{N}_l and \mathbf{E} . Since the matrix \mathbf{E} is known and $\text{rank}(\mathbf{E}) = S_l$, its inverse exists. Hence, the numbers of moles matrix \mathcal{N}_l can be computed from Eq. (5.30) as follows:

$$\mathcal{N}_l^T = (\mathbf{E}^T)^+ \mathbf{A}_v^T. \quad (\text{A.19})$$

The h th column of the \mathcal{N}_l^T corresponds to the S_l number of moles at the t_h time instant, i.e. $\mathbf{n}_l(t_h)$. Since Conditions (i) and (ii) satisfy, Theorem 3.1 can be applied to $\mathbf{n}_l(t_h)$ compute the extents of reaction and mass transfer. For H observations, it leads to the matrices \mathbf{X}_r and $\mathbf{X}_{m,l}$. Hence, the corollary is proven.

A.11 Proof of Corollary 5.6

Since $\mathbf{u}_{in,l}(t)$, $u_{out,l}$, and $m_l(t)$ are measured, the matrices $\mathbf{X}_{in,l}$ and $\mathbf{\Lambda}_l$ can be computed. Using the computed matrices $\mathbf{X}_{in,l}$ and $\mathbf{\Lambda}_l$, and the measured \mathbf{A}_{in} and \mathbf{a}_0 , the spectral data in RMV-form \mathbf{H}_{rm} can be computed in Step 1 from \mathbf{A}_v .

Since all transferring species react, $\mathbf{W}_{m,nr} = \mathbf{0}_{p_m \times S_{nr}}$. Hence, $\mathbf{W}_{m,l}^T \mathbf{E} = [\mathbf{w}_{m,l}^T \mathbf{0}] \begin{bmatrix} \mathbf{E} \\ \mathbf{E}_{nr} \end{bmatrix} = \mathbf{W}_{m,l}^T \mathbf{E}$. Note that $\mathbf{N}\mathbf{E} = [\mathbf{N} \mathbf{0}_{R \times S_{nr}}] \begin{bmatrix} \mathbf{E} \\ \mathbf{E}_{nr} \end{bmatrix} = \mathbf{N}\mathbf{E}$. Hence, \mathbf{H}_{rm} contains the contributions of the extents of reaction and mass transfer only. Since the pure-component spectra of reacting species are known, and $\text{rank}([\mathbf{N}^T \mathbf{W}_{m,l}]) = R + p_m$, the inverse of \mathbf{E}_{rm} exists. Hence, the matrix of the extents of reaction and mass transfer \mathbf{X}_{rm} can be computed in Step 2 from \mathbf{H}_{rm} . This proves the corollary.

Appendix B

Modeling specificities for gas-phase and liquid-phase reaction systems

The specificities such as 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:

$$\begin{aligned}\mathbf{r}(t) &= \mathbf{r}_L(\mathbf{c}(t), T(t)), & V(t) &= \frac{m(t)}{\rho(t)} \\ \text{with } \mathbf{c}(t) &= \frac{\mathbf{n}(t)}{V(t)}, & \rho(t) &= \rho_L(\mathbf{n}(t), T(t)), \\ \dot{T}(t) &= f_L(T(t), \mathbf{n}(t), u_{in}(t), u_{out}(t), Q_{ext}(t)), & T(0) &= T_0,\end{aligned}\tag{B.1}$$

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, $u_{out}(t)$ 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. (2.28) which reduces to $u_{out}(t) = \mathbf{1}_p^T \mathbf{u}_{in}(t)$ 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:

$$\begin{aligned} \mathbf{r}(t) &= \mathbf{r}_G(\mathcal{P}(t), T(t)) \\ \text{with } \mathcal{P}(t) &= \mathcal{P}_G(\mathbf{n}(t), T(t)), \quad \mathcal{P}_t(t) = \mathbf{1}_S^\top \mathcal{P}(t) \\ \dot{T}(t) &= f_G(T(t), \mathbf{n}(t), \mathcal{P}_t(t), u_{in}(t), u_{out}(t), Q_{ext}(t)), \quad T(0) = T_0, \end{aligned} \tag{B.2}$$

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

Appendix C

Algorithm to compute \mathbf{S} , \mathbf{M} and \mathbf{Q}

The algorithm assumes $\text{rank}([\mathbf{N}^T \ \mathbf{W}_{in}]) = R + p$, although it can easily be extended to the case of $\text{rank}([\mathbf{N}^T \ \mathbf{W}_{in}]) < R + p$. 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 A.1.

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

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

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

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

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

Appendix D

Nonlinear transformation of the numbers of moles to reaction variants, flow variants and invariants

The construction of the linear transformations to the extents of reaction, mass transfer and flow proposed in Chapters 2 and 3 requires information regarding the initial conditions in addition to the stoichiometry and the inlet composition. Hence, in contrast to the nonlinear transformation in [75], the proposed linear transformation is not *one-to-one*. In this appendix, novel *one-to-one* nonlinear transformations will be proposed using only information regarding the stoichiometry, and the inlet composition, i.e. independent of the initial conditions, which transform the number of moles vector to reaction variants, mass-transfer variants, inlet-flow variants, outlet-flow variant, and invariant states. First, a nonlinear transformation proposed by Srinivasan et al. [75] will be revisited. Then, a *novel one-to-one nonlinear* transformation will be proposed for homogeneous reaction systems. This novel nonlinear transformation will be extended to gas–liquid reaction systems.

D.1 Homogeneous reaction systems

In this section, one-to-one nonlinear transformations of the numbers of moles will be discussed for homogeneous reactors. First, the nonlinear transformation proposed by Srinivasan et al. [75] will be revisited and then, a novel nonlinear transformation will be proposed.

D.1.1 Four-way decomposition: Reaction variants, inlet-flow variants, outlet-flow variant, and invariants using a nonlinear transformation proposed by Srinivasan et al. [75]

Srinivasan et al. [75] proposed a nonlinear transformation of the numbers of moles into reaction variants, flow variants, and invariants using the continuity equation (2.2). The following theorem introduces this one-to-one nonlinear transformation of the numbers of moles.

Theorem D.1 (Nonlinear transformation of $\mathbf{n}(t)$)

If $\text{rank}([\mathbf{N}^T, \mathbf{W}_{in}]) = (R + p)$, then a diffeomorphism $\mathcal{T} : [\frac{\mathbf{n}}{m}] \leftrightarrow [\frac{\mathbf{x}}{\lambda}]$ exists that transforms model Eqs. (2.1)-(2.2) into:

$$\begin{aligned} \dot{\mathbf{x}}_r &= \frac{h(\mathbf{x}_{in})}{\rho(\mathbf{x})} \mathbf{r}(\mathbf{x}), & \mathbf{x}_r(0) &= \eta \mathbf{S}^T \mathbf{n}_0, & (\text{reaction variants}) \\ \dot{\mathbf{x}}_{in} &= \mathbf{u}_{in}/\lambda, & \mathbf{x}_{in}(0) &= \eta \mathbf{M}^T \mathbf{n}_0, & (\text{flow variants}) \\ \dot{\mathbf{x}}_{iv} &= \mathbf{0}_{S-R-p}, & \mathbf{x}_{iv}(0) &= \eta \mathbf{Q}^T \mathbf{n}_0, & (\text{invariants}) \\ \dot{\lambda} &= -u_{out}/h(\mathbf{x}_{in}), & \lambda(0) &= 1/\eta, & (\text{flow variant}) \end{aligned} \quad (\text{D.1})$$

where

$$h(\mathbf{x}_{in}) = \eta (m_0 - \mathbf{1}_p^T \mathbf{M}^T \mathbf{n}_0) + \mathbf{1}_p^T \mathbf{x}_{in}, \quad (\text{D.2})$$

and where \mathbf{x}_r , \mathbf{x}_{in} and λ are the reaction variants, the flow variants, and the outlet-flow variant of dimensions R , p and 1, respectively, while \mathbf{x}_{iv} are the reaction and flow invariants of dimension $(S - R - p)$. η is a nonzero arbitrary constant, and \mathbf{r} the R -dimensional reaction rate vector expressed in terms of \mathbf{x} . The matrices \mathbf{S} , \mathbf{M} and \mathbf{Q} are computed using the algorithm given in Appendix C

The transformation to normal form \mathcal{T} is one-to-one and can be written as follows using $g(\mathbf{n}, m) = \eta (m_0 - \mathbf{1}_p^T \mathbf{M}^T \mathbf{n}_0)/(m - \mathbf{1}_p^T \mathbf{M}^T \mathbf{n})$:

$$\begin{bmatrix} \mathbf{n} \\ m \end{bmatrix} \rightarrow \begin{bmatrix} \mathbf{x} \\ \lambda \end{bmatrix} : \quad \begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{in} \\ \mathbf{x}_{iv} \\ \lambda \end{bmatrix} = \begin{bmatrix} g(\mathbf{n}, m) \mathbf{S}^T \mathbf{n} \\ g(\mathbf{n}, m) \mathbf{M}^T \mathbf{n} \\ g(\mathbf{n}, m) \mathbf{Q}^T \mathbf{n} \\ 1/g(\mathbf{n}, m) \end{bmatrix} \quad (\text{D.3})$$

$$\begin{bmatrix} \mathbf{x} \\ \lambda \end{bmatrix} \rightarrow \begin{bmatrix} \mathbf{n} \\ m \end{bmatrix} : \quad \begin{bmatrix} \mathbf{n} \\ m \end{bmatrix} = \begin{bmatrix} \lambda (\mathbf{N}^T \mathbf{x}_r + \mathbf{W}_{in} \mathbf{x}_{in} + \mathbf{Q} \mathbf{x}_{iv}) \\ \lambda h(\mathbf{x}_{in}) \end{bmatrix}. \quad (\text{D.4})$$

(See Proof in Appendix A of Srinivasan et al. [75])

Note that the transformed states in Eq. (D.1) are abstract mathematical quantities that are devoid of any physical meaning.

D.1.2 Four-way decomposition: Reaction variants, inlet-flow variants, outlet-flow variant, and invariants using a nonlinear transformation in this thesis

An alternative *one-to-one novel nonlinear transformation* will be developed next that does not require the continuity equation or information regarding the initial conditions. The linear transformation in Theorem 2.1 decomposes the numbers of moles into reaction variants, inlet-flow variants and reaction and inlet-flow invariants, respectively. The reaction and inlet-flow invariants \mathbf{z}_{iv} in Eq. (2.14) vary with the outlet when

$u_{out} > 0$. In this section, $\mathbf{z}_{iv}(t)$ will be transformed nonlinearly to result in *reaction and flow invariants* when $u_{out} > 0$. By selecting the scalar variable $\lambda(t) = z_{iv,i}(t)$ with $z_{iv,i}(0) \neq 0$ and transforming the remaining reaction and inlet-flow invariants $z_{iv,j}(t)$, $\forall j = 1, \dots, S - R - p - 1$, $j \neq i$, nonlinearly as follows:

$$\mathbf{z}_{iv} \longrightarrow \begin{bmatrix} \mathbf{x}_{iv} \\ \lambda \end{bmatrix} : \begin{bmatrix} \{x_{iv,j}\} \\ \lambda \end{bmatrix} = \begin{bmatrix} \{\frac{z_{iv,j}}{\lambda}\} \\ z_{iv,i} \end{bmatrix}, \quad (\text{D.5})$$

\mathbf{x}_{iv} becomes an $(S - R - p - 1)$ -dimensional vector of *reaction and flow invariants*. The scalar dimensionless λ is the outlet-flow variant. The nonlinear transformation is detailed in the next theorem. The reaction and inlet-flow variants \mathbf{z}_r and \mathbf{z}_{in} are denoted \mathbf{x}_r and \mathbf{x}_{in} , respectively.

Theorem D.2 (Nonlinear transformation of $\mathbf{n}(t)$ proposed in this thesis)

Consider a homogeneous reaction system involving S species, R independent reactions, p independent inlets and one outlet, and let $\text{rank}([\mathbf{N}^T \mathbf{W}_{in}]) = R + p$. Then, there exists a diffeomorphism $\Psi: [\mathbf{n}] \leftrightarrow [\tilde{\mathbf{x}}]$,

$$[\mathbf{n}] \rightarrow \begin{bmatrix} \mathbf{x} \\ \lambda \end{bmatrix} : \begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{in} \\ \mathbf{x}_{iv} \\ \lambda \end{bmatrix} = \begin{bmatrix} \mathbf{S}^T \mathbf{n} \\ \mathbf{M}^T \mathbf{n} \\ g(\mathbf{n}) \mathbf{Q}_{iv}^T \mathbf{n} \\ \frac{1}{g(\mathbf{n})} \end{bmatrix}, \quad (\text{D.6})$$

$$\begin{bmatrix} \mathbf{x} \\ \lambda \end{bmatrix} \rightarrow [\mathbf{n}] : \quad \mathbf{n}(t) = \mathbf{N}^T \mathbf{x}_r(t) + \mathbf{W}_{in} \mathbf{x}_{in}(t) + \mathbf{Q} \begin{bmatrix} 1 \\ \mathbf{x}_{iv} \end{bmatrix} \lambda(t), \quad (\text{D.7})$$

where $g(\mathbf{n})$ is defined as follows:

$$g(\mathbf{n}) = \begin{cases} 1/\mathbf{q}^T \mathbf{n} & \forall \mathbf{q}^T \mathbf{n} \neq 0, \\ \eta & \forall \mathbf{q}^T \mathbf{n} = 0. \end{cases} \quad (\text{D.8})$$

The diffeomorphism Ψ transforms Eq. (2.1) to the following form:

$$\begin{aligned} \dot{\mathbf{x}}_r &= V\mathbf{r} - \frac{u_{out}}{m} \mathbf{x}_r, & \mathbf{x}_r(0) &= \mathbf{S}^T \mathbf{n}_0, & (\text{reaction variants}) \\ \dot{\mathbf{x}}_{in} &= \mathbf{u}_{in} - \frac{u_{out}}{m} \mathbf{x}_{in}, & \mathbf{x}_{in}(0) &= \mathbf{M}^T \mathbf{n}_0, & (\text{inlet-flow variants}) \\ \dot{\mathbf{x}}_{iv} &= \mathbf{0}_{S-R-p-1}, & \mathbf{x}_{iv}(0) &= g(\mathbf{n}_0) \mathbf{Q}_{iv}^T \mathbf{n}_0, & (\text{invariants}) \\ \dot{\lambda} &= -\frac{u_{out}}{m} \lambda, & \lambda(0) &= 1/g(\mathbf{n}_0), & (\text{outlet-flow variant}) \end{aligned} \quad (\text{D.9})$$

where \mathbf{x}_r , \mathbf{x}_{in} and λ are the reaction variants, the inlet-flow variants, and the outlet-flow variant of dimensions R , p and 1, respectively, while \mathbf{x}_{iv} are the reaction and flow invariants of dimension $(S - R - p - 1)$. Without loss of generality, \mathbf{q} is an S -dimensional vector corresponding to one column of \mathbf{Q} , \mathbf{Q}_{iv} is $S \times (S - R - p - 1)$ -dimensional matrix

corresponding to the remaining $(S - R - p - 1)$ columns of \mathbf{Q} , and η is a non-zero arbitrary real constant.

Proof: The proof of Theorem D.2 will be given in three parts. The first part proving that there exists the linear transformation of Eq. (2.1) to Eq. (2.14), is already given in Theorem 2.1.

In the second part of the proof, it will be shown that $g(\mathbf{n})$ is always defined. Let define $a \equiv \mathbf{q}^T \mathbf{n}$ by choosing $\mathbf{q}^T \mathbf{n}_0 \neq 0$. Then, $a(t) = \lambda(t)$ and by differentiating $a(t)$, it follows that $\dot{a} = \dot{\lambda} = -\frac{u_{out}}{m} a(t)$. Since $a(0) = \mathbf{q}^T \mathbf{n}_0 \neq 0$ and u_{out} and m are positive, $a(t) \neq 0$ for all time t . If one does not find any $\mathbf{q}^T \mathbf{n} \neq 0$, i.e. $\mathbf{q}^T \mathbf{n} = 0$, then by choosing $a(t) = \eta$, $g(\mathbf{n}) = \eta$, η is any arbitrary non-zero constant. Then, since $\mathbf{x}_{iv}(0) = \mathbf{0}_{S-R-v}$, $\mathbf{x}_{iv}(t) = \mathbf{0}_{S-R-v}$ for all t and $\dot{\lambda}(t) = 0$ with $\lambda(0) = 1/\eta$.

In the last part of the proof, Eq. (D.7) is derived. The states \mathbf{x} and λ in Theorem D.2 can be written in terms of \mathbf{z} as follows:

$$\mathbf{z}_r = \mathbf{x}_r, \quad \mathbf{z}_{in} = \mathbf{x}_{in}, \quad \mathbf{z}_{iv} = \begin{bmatrix} \lambda \mathbf{x}_{iv} \\ \lambda \end{bmatrix} \quad (\text{D.10})$$

Using Eq. (2.15) in Theorem 2.1 and Eq. (D.10), the numbers of moles \mathbf{n} in the reactor at time t can be computed as follows:

$$\begin{aligned} \mathbf{n}(t) &= \mathbf{N}^T \mathbf{z}_r(t) + \mathbf{W}_{in} \mathbf{z}_{in}(t) + \mathbf{Q} \mathbf{z}_{iv}(t) \\ &= \mathbf{N}^T \mathbf{x}_r(t) + \mathbf{W}_{in} \mathbf{x}_{in}(t) + \mathbf{Q} \begin{bmatrix} 1 \\ \mathbf{x}_{iv} \end{bmatrix} \lambda(t) \end{aligned} \quad (\text{D.11})$$

Hence, the theorem is proved. \square

Remarks.

1. The reaction variants and the inlet-flow variants in Theorem D.2 and those in Theorem 2.1 are same, i.e. $\mathbf{x}_r = \mathbf{z}_r$ and $\mathbf{x}_{in} = \mathbf{z}_{in}$.
2. The transformed reaction system is of dimension $(R + p + 1)$ and not S . Since the dynamics of $(S - R - p - 1)$ invariant states \mathbf{x}_{iv} are removed, \mathbf{x}_{iv} are constant.
3. The nonlinear transformation decomposes the reaction and inlet-flow invariants \mathbf{z}_{iv} into the invariants \mathbf{x}_{iv} and the outlet-flow variant λ . Hence, \mathbf{x}_r evolves in the R -dimensional space $\mathbf{N}^T \mathbf{S}^T$, \mathbf{x}_{in} in the p -dimensional space $\mathbf{W}_{in} \mathbf{M}^T$, \mathbf{x}_{iv} in $(S - R - p - 1)$ -dimensional space $\mathbf{Q}_{iv} \mathbf{Q}_{iv}^T$, and λ evolves in the one dimensional space $\mathbf{q} \mathbf{q}^T$. Note that $\mathbf{N}^T \mathbf{S}^T + \mathbf{W}_{in} \mathbf{M}^T + \mathbf{Q}_{iv} \mathbf{Q}_{iv}^T + \mathbf{q} \mathbf{q}^T = \mathbf{I}_S$. The nonlinear transformation of Theorem D.2 is illustrated in Figure D.1.
4. If $\mathbf{q}^T \mathbf{n} = 0$, then $g(\mathbf{n})$ needs to be redefined. $\mathbf{q}^T \mathbf{n} = 0$ indicates that the reaction and inlet-flow invariants (\mathbf{z}_{iv}) are equal to zero. In such a case, $g(\mathbf{n})$ be defined by choosing any nonzero arbitrary constant η and the transformation in Theorem D.2 holds with nonzero constant η .
5. The nonlinear transformation proposed in Theorem D.1 is different from the one proposed in Theorem D.2. In contrast to the nonlinear transformation of [75], the

construction of the nonlinear transformation in Theorem D.2 does not use the continuity equation. Moreover, the reaction and flow variants in [75] tend to infinity with time for continuous reactor if the meta parameter η is not chosen properly. However, this is not the case with the transformed states in Theorem D.2 since the reaction and inlet-flow variants are not affected by the choice of η .

6. Since the linear transformation (2.18) is not one-to-one, a transformation constructed for given initial conditions cannot be applied to a different set of initial conditions. In contrast, the nonlinear transformation in Theorems D.1–D.2 do not require information regarding the initial condition \mathbf{n}_0 and they can be applied to a different set of initial conditions.
7. The transformed states in Theorem 2.2 are the extents of reaction and flows, whereas the transformed states in Theorem D.2 are abstract mathematical quantities that are devoid of any physical meaning.
8. The nonlinear and linear transformations in Theorems D.2 and 2.2 both lead to $(R+p+1)$ variant states. However, the linear transformation leads to the $(S-R-p)$ invariant states, while the nonlinear transformation leads to the $(S-R-p-1)$ invariant states. Note that the invariant states obtained by the linear and nonlinear transformations live in the $(S-R-p-1)$ -dimensional subspace.
9. The nonlinear transformation is *one-to-one*. This transformation is particularly well suited for analysis and control studies that deal such as feedback linearization, computation of flat outputs, and nonlinear analysis in general [75, 81].

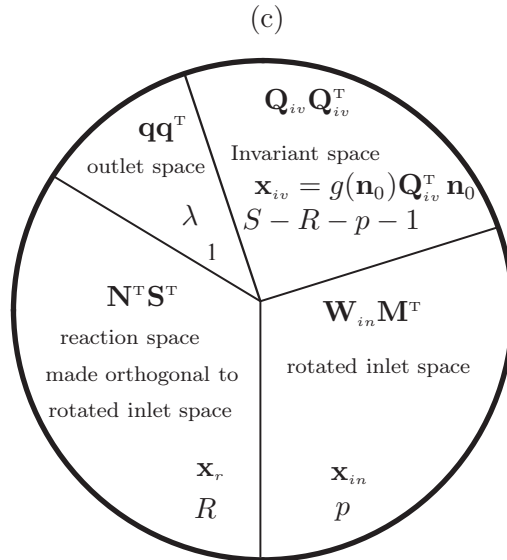


Figure D.1 Nonlinear transformation of the S -dimensional space of numbers of moles into an R -dimensional reaction space, a p -dimensional inlet-flow space, an $(S-R-p-1)$ -dimensional invariant space, and a one-dimensional outlet-flow space. All spaces are orthogonal to each other with $\mathbf{N}^T \mathbf{S}^T + \mathbf{W}_{in} \mathbf{M}^T + \mathbf{Q}_{iv} \mathbf{Q}_{iv}^T + \mathbf{q} \mathbf{q}^T = \mathbf{I}_S$.

D.2 Gas–liquid reaction systems

The aim of this section is to extend the *one-to-one* nonlinear transformation proposed in this thesis for homogeneous reaction systems to G–L reaction systems. The extension to G–L reaction systems leads to the concept of mass–transfer variants. The mass–transfer variants can be defined as follows:

Definition D.1 (Mass-transfer variants)

Any set of p_m linearly independent variables that evolve in the mass–transfer space constitutes a mass–transfer variant set.

The nonlinear transformation will be developed separately for $\mathbf{n}_l(t)$ and $\mathbf{n}_g(t)$ in Eqs. (3.10) and (3.9):

- Nonlinear transformation of $\mathbf{n}_l(t)$ to reaction variants, mass-transfer variants, inlet-flow variants, outlet-flow variant, and invariants in the liquid phase.
- Nonlinear transformation of $\mathbf{n}_g(t)$ to mass-transfer variants, inlet-flow variants, outlet-flow variant, and invariants in the gas phase.

D.2.1 Five-way decomposition of $\mathbf{n}_l(t)$: Reaction, mass–transfer, inlet-flow and outlet-flow variants, and invariants using a nonlinear transformation

The next theorem introduces a nonlinear transformation of the numbers of moles in the liquid phase to reaction variants, mass–transfer variants, inlet-flow variants and outlet-flow variant, and reaction, mass–transfer and flow invariants.

Theorem D.3 (Nonlinear transformation of $\mathbf{n}_l(t)$)

Consider the liquid phase of the G–L reaction system given by Eq. (3.16) involving S_l species, R independent reactions, p_l independent inlets, one outlet, and p_m mass transfers between the gas and liquid phases. If $\text{rank}([\mathbf{N}^T \ \bar{\mathbf{W}}_{in,l}]) = R + p_l + p_m$, there exists a diffeomorphism $\Psi: [\mathbf{n}_l] \leftrightarrow [\mathbf{x}_l]$ such that:

$$[\mathbf{n}_l] \rightarrow [\mathbf{x}_l] : \begin{bmatrix} \mathbf{x}_r \\ \bar{\mathbf{x}}_{in,l} \\ \mathbf{x}_{iv,l} \\ \lambda_l \end{bmatrix} = \begin{bmatrix} \mathbf{S}_l^T \mathbf{n}_l \\ \bar{\mathbf{M}}_l^T \mathbf{n}_l \\ g_l(\mathbf{n}_l) \mathbf{Q}_{iv,l}^T \mathbf{n}_l \\ 1/g_l(\mathbf{n}_l) \end{bmatrix}, \quad (\text{D.12})$$

with

$$g_l(\mathbf{n}_l) = \begin{cases} 1/\mathbf{q}_l^T \mathbf{n}_l & \forall \mathbf{q}_l^T \mathbf{n}_l \neq 0, \\ \eta & \forall \mathbf{q}_l^T \mathbf{n}_l = 0, \end{cases} \quad (\text{D.13})$$

$$(\text{D.14})$$

and $\mathbf{S}_l^T = \mathbf{N}_l^{T+} (\mathbf{I}_{S_l} - \bar{\mathbf{W}}_{in,l} \bar{\mathbf{M}}_l^T)$. The diffeomorphism transforms \mathbf{n}_l in Eq. (3.16) to the reaction variants \mathbf{x}_r , the extended-inlet variants $\bar{\mathbf{x}}_{in,l}$, the outlet flow variant λ_l , and the

invariants $\mathbf{x}_{iv,l}$ in the liquid phase. The extended-inlet variants $\bar{\mathbf{x}}_{in,l}$ can be expressed in terms of the mass-transfer variants in the liquid phase $\mathbf{x}_{m,l}$, and the inlet-flow variants in the liquid phase $\mathbf{x}_{in,l}$, thus leading to the following transformed state equations:

$$\begin{aligned}
 \dot{\mathbf{x}}_{r,l} &= V_l \mathbf{r} - \frac{u_{out,l}}{m_l} \mathbf{x}_{r,l}, & \mathbf{x}_{r,l}(0) &= \mathbf{S}_l^T \mathbf{n}_{l0}, \\
 \dot{\mathbf{x}}_{m,l} &= \zeta - \frac{u_{out,l}}{m_l} \mathbf{x}_{m,l}, & \mathbf{x}_{m,l}(0) &= \mathbf{M}_{m,l}^T \mathbf{n}_{l0}, \\
 \dot{\mathbf{x}}_{in,l} &= \mathbf{u}_{in,l} - \frac{u_{out,l}}{m_l} \mathbf{x}_{in,l}, & \mathbf{x}_{in,l}(0) &= \mathbf{M}_{in,l}^T \mathbf{n}_{l0}, \\
 \dot{\mathbf{x}}_{iv,l} &= \mathbf{0}_{S_l-R-p_m-p_l-1}, & \mathbf{x}_{iv,l}(0) &= g_l(\mathbf{n}_{l0}) \mathbf{Q}_{iv,l}^T \mathbf{n}_{l0}, \\
 \dot{\lambda}_l &= -\frac{u_{out,l}}{m_l} \lambda_l, & \lambda_l(0) &= \frac{1}{g_l(\mathbf{n}_{l0})},
 \end{aligned} \tag{D.15}$$

where $\mathbf{M}_{m,l}$ is the $(S_l \times p_m)$ -dimensional matrix corresponding to the first p_m columns of $\bar{\mathbf{M}}_l$, while $\mathbf{M}_{in,l}$ is the $(S_l \times p_l)$ -dimensional matrix corresponding to the last p_l columns of $\bar{\mathbf{M}}_l$. Without loss of generality, \mathbf{q}_l is an S_l -dimensional vector corresponding to one column of \mathbf{Q}_l , $\mathbf{Q}_{iv,l}$ is $S_l \times (S_l - R - p_m - p_l - 1)$ -dimensional matrix corresponding to the remaining $(S_l - R - p_m - p_l - 1)$ columns of \mathbf{Q}_l . The matrices \mathbf{S}_l , $\bar{\mathbf{M}}_l$ and \mathbf{Q}_l are computed using the algorithm given in Appendix C. The back transformation Ψ^{-1} : $\begin{bmatrix} \mathbf{x}_l \\ \lambda_l \end{bmatrix} \rightarrow \mathbf{n}_l$ leads to the reconstruction of the numbers of moles \mathbf{n}_l from the states \mathbf{x}_l and λ_l as follows:

$$\begin{bmatrix} \mathbf{x}_l \\ \lambda_l \end{bmatrix} \rightarrow \begin{bmatrix} \mathbf{n}_l \end{bmatrix} : \mathbf{n}_l(t) = \mathbf{N}^T \mathbf{x}_r(t) + \mathbf{W}_{in,l} \mathbf{x}_{in,l}(t) + \mathbf{W}_{m,l} \mathbf{x}_{m,l}(t) + \mathbf{Q}_l \begin{bmatrix} 1 \\ \mathbf{x}_{iv,l} \end{bmatrix} \lambda_l(t) \tag{D.16}$$

(Proof follows from Theorem D.2.)

Interpretation of the nonlinear transformation.

The decomposition of the S_l -dimensional space into subspaces is illustrated in Figure D.2. The transformation can be interpreted in two steps. The first step is illustrated in Figure 3.3a.

In the second step, the reaction, mass-transfer and inlet-flow invariants space $\mathbf{Q}_l \mathbf{Q}_l^T$ is partitioned into the $(S - R - p_m - p_l - 1)$ -dimensional invariant space $\mathbf{Q}_{iv,l} \mathbf{Q}_{iv,l}^T$ and the one-dimensional outlet space $\mathbf{q}_l \mathbf{q}_l^T$, as shown in Figure D.2. Then, using the outlet variant λ_l , the nonlinear transformation in Eq. (D.12) is constructed that generates the invariant states $\mathbf{x}_{iv,l}$ in the invariant space $\mathbf{Q}_{iv,l} \mathbf{Q}_{iv,l}^T$.

The reaction variants \mathbf{x}_r evolve in the R -dimensional rotated reaction space $\mathbf{N}^T \mathbf{S}_l^T$, the mass-transfer variants $\mathbf{x}_{m,l}$ in the p_m -dimensional rotated mass-transfer space $\mathbf{W}_{m,l} \mathbf{M}_{m,l}^T$, the inlet-flow variants $\mathbf{x}_{in,l}$ in the p_l -dimensional rotated inlet space $\mathbf{W}_{in,l} \mathbf{M}_{in,l}^T$, and the outlet variant λ_l in the one-dimensional space $\mathbf{q}_l \mathbf{q}_l^T$. The transformed states

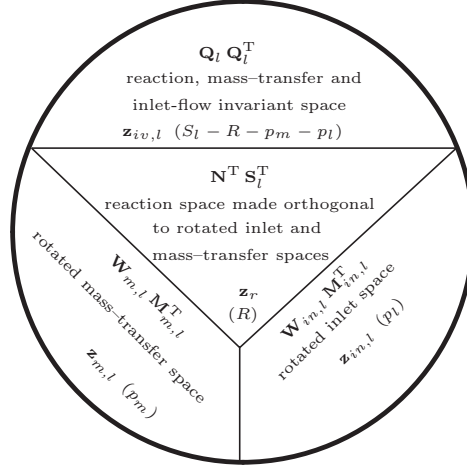


Figure D.2 Mathematical five-way decomposition of $\mathbf{n}_l(t)$ into four orthogonal variants spaces and one orthogonal invariant space using a nonlinear transformation: an R -dimensional reaction sapce, a p_m -dimensional mass-transfer space, a p_l -dimensional inlet space, an $(S_l - R - p_l - p_m - 1)$ -dimensional invariant space, and a one-dimensional outlet variant space.

in Theorem D.3 are abstract mathematical quantities that are devoid of any physical meaning.

D.2.2 Four-way decomposition of $\mathbf{n}_g(t)$: Mass-transfer, inlet-flow and outlet-flow variants, and invariants using a nonlinear transformation

The next corollary introduces a transformation of the numbers of moles in the gas phase to mass-transfer variants, flow variants, and mass-transfer and flow invariants.

Corollary D.1 (Nonlinear transformation of $\mathbf{n}_g(t)$)

Consider the gas phase of the G – L reaction system given by Eq. (3.15) involving S_g species, p_g independent inlets, one outlet, and p_m mass transfers between the gas and liquid phases. If $\text{rank}(\bar{\mathbf{W}}_{in,g}) = p_g + p_m$, there exists a diffeomorphism $\Psi: [\mathbf{n}_g] \leftrightarrow [\mathbf{x}_g]$ such that:

$$[\mathbf{n}_g] \rightarrow \begin{bmatrix} \mathbf{x}_g \\ \lambda_g \end{bmatrix} : \quad \begin{bmatrix} \bar{\mathbf{x}}_{in,g} \\ \mathbf{x}_{iv,g} \\ \lambda_g \end{bmatrix} = \begin{bmatrix} \bar{\mathbf{M}}_g^T \mathbf{n}_g \\ g_g(\mathbf{n}_g) \mathbf{Q}_{iv,g}^T \mathbf{n}_g \\ 1/g_g(\mathbf{n}_g) \end{bmatrix} \quad (\text{D.17})$$

with

Appendix E

Asymptotic observers in homogeneous and gas–liquid reaction systems

E.1 Homogeneous reaction systems

In homogeneous reaction systems, the parametric uncertainties and nonlinearities of the process models lie in the reaction kinetics. The known stoichiometries and the knowledge of reaction invariants can be used to design asymptotic observers without knowledge of reaction kinetics using a subset of concentration measurements [11, 27, 28, 20, 75]. The objective of this section is to design asymptotic observers using *the extents of flows* (\mathbf{x}_{in} and λ) similar to those proposed in [11, 27, 75].

The trajectories of the numbers of moles in homogeneous reaction systems are given by Eq. (2.1). The parameter uncertainties and nonlinearities in the process models residing in $V(t)\mathbf{r}(t)$, called reaction terms, are usually unknown. The transformation in Eq. (2.18) separates the contributions of the reaction terms from the inlet and outlet flows. Hence, if the contribution of the reaction terms can indirectly be measured through concentration measurements of some species, then the unmeasured concentrations in homogeneous reaction systems can be estimated using an asymptotic observer.

To design asymptotic observers, the following assumptions are introduced: (E1) the stoichiometric matrix \mathbf{N} and the inlet matrix \mathbf{W}_{in} are known; (E2) the concentrations of S_a species (\mathbf{c}_a) are measured such that $\text{rank}(\mathbf{N}_a) = R$ where \mathbf{N}_a is the $R \times S_a$ -dimensional stoichiometric matrix corresponding to the measured species; (E3) \mathbf{u}_{in} , u_{out} and V are measured without errors; and (E4) an estimate of the initial concentrations ($\hat{\mathbf{c}}_0$) of species is available. Then, the extents of reaction (\mathbf{x}_r) can be estimated from the measured concentrations, volume, inlet and outlet flowrates as shown in Eq. (4.10).

Hence, the $S_u = (S - S_a)$ unmeasured numbers of moles \mathbf{n}_u and concentrations $\mathbf{c}_u = \mathbf{n}_u/V$ can be computed from Eq. (4.11) and other measurements. The details are explained in the following propositions.

Proposition E.1 (Asymptotic observers: Homogeneous reaction systems)

If Assumptions (E1)–(E4) are valid for a homogeneous reaction system described by Eq. (2.1), then the following equations:

$$\begin{aligned} \dot{\hat{\mathbf{x}}}_{in} &= \mathbf{u}_{in} - \frac{u_{out}}{m} \hat{\mathbf{x}}_{in}, & \hat{\mathbf{x}}_{in}(0) &= \mathbf{0}_p, \\ \dot{\hat{\lambda}} &= -\frac{u_{out}}{m} \hat{\lambda}, & \hat{\lambda}(0) &= 1, \end{aligned} \tag{E.1}$$

and

$$\hat{\mathbf{c}}_u = \boldsymbol{\kappa} \mathbf{c}_a + \boldsymbol{\kappa}_W \hat{\mathbf{x}}_{in} + \hat{\boldsymbol{\kappa}}_{n0} \hat{\lambda}, \quad (\text{E.2})$$

form an asymptotic observer for the S_u unmeasured species, where $\hat{\mathbf{c}}_u$ is an S_u -dimensional vector of estimated concentrations of the unmeasured species, $\boldsymbol{\kappa} = \frac{\mathbf{N}_u^T \mathbf{N}_a^{T+}}{V}$, $\boldsymbol{\kappa}_W = \frac{(\mathbf{W}_{in,u} - \boldsymbol{\kappa} \mathbf{W}_{in,a})}{V}$, $\hat{\boldsymbol{\kappa}}_{n0} = \frac{(\hat{\mathbf{n}}_{0,u} - \boldsymbol{\kappa} \mathbf{n}_{0,a})}{V}$, and the subscripts a and u denote quantities corresponding to the S_a available (measured) and S_u unavailable (unmeasured) species, respectively.

The vector of estimation errors of the unmeasured concentrations, $\mathbf{e}_u = \mathbf{c}_u - \hat{\mathbf{c}}_u$, with \mathbf{c}_u the true unmeasured concentrations, is given by

$$\mathbf{e}_u = (\mathbf{N}_u^T \frac{\mathbf{x}_r}{V} - \boldsymbol{\kappa} \mathbf{c}_a) + \boldsymbol{\kappa}_W (\mathbf{x}_{in} - \hat{\mathbf{x}}_{in}) + \boldsymbol{\kappa}_{n0} \lambda - \hat{\boldsymbol{\kappa}}_{n0} \hat{\lambda}. \quad (\text{E.3})$$

If at least one of the inlet flowrates is nonzero for a long enough time, then the estimated errors of the unmeasured concentrations are asymptotically stable and converge to zeros.

Proof: The concentrations can be partitioned into measured and unmeasured concentrations and expressed in terms of \mathbf{x}_r , \mathbf{x}_{in} and λ as follows:

$$\mathbf{c} = \begin{bmatrix} \mathbf{c}_a \\ \mathbf{c}_u \end{bmatrix} = \frac{1}{V} \begin{bmatrix} \mathbf{n}_a \\ \mathbf{n}_u \end{bmatrix} = \begin{bmatrix} \mathbf{N}_a^T \\ \mathbf{N}_u^T \end{bmatrix} \mathbf{x}_r + \begin{bmatrix} \mathbf{W}_{in,a} \\ \mathbf{W}_{in,u} \end{bmatrix} \mathbf{x}_{in} + \begin{bmatrix} \mathbf{n}_{0,a} \\ \mathbf{n}_{0,u} \end{bmatrix} \lambda. \quad (\text{E.4})$$

Since the unique left pseudo-inverse of \mathbf{N}_a^T exists, the extents of inlet \mathbf{x}_{in} and the outlet variant λ can be computed from the measured mass flowrates. The substitution of Eq. (4.10) into the unmeasured concentrations (\mathbf{c}_u) in Eq. (E.4) leads to Eq. (E.2).

Since the concentrations \mathbf{c}_a do not contain any error by assumption, the vector of estimation errors $\mathbf{e}_u = \mathbf{c}_u - \hat{\mathbf{c}}_u$ can be expressed as described in Eq. (E.3). Since \mathbf{u}_{in} , \mathbf{u}_{out} and V are measured without any error by assumption, the error dynamics are given by:

$$\dot{\mathbf{e}}_u = -\left(\frac{u_{out}}{m} + \frac{\dot{V}}{V}\right) \mathbf{e}_u, \quad (\text{E.5})$$

$$= -\left(\frac{u_{out}}{m} + \frac{\dot{\rho}}{\rho}\right) \mathbf{e}_u. \quad (\text{E.6})$$

The integration of Eq. (E.6) leads to:

$$\mathbf{e}_u(t) = \frac{\mathbf{e}_u(0)\rho(t)}{\rho_0} \exp\left(\int -\frac{\mathbf{1}^T \mathbf{u}_{in}}{m} dt\right), \quad (\text{E.7})$$

where $\mathbf{e}_u(0)$ is the S_u -dimensional vector of errors in the initial conditions, $\rho(t)$ is the density at time t and $\exp(\cdot)$ indicates a exponential function. If at least one of the inlet flowrates is nonzero for a long enough time (i.e. $t \rightarrow \infty$), then $\frac{\mathbf{1}^T \mathbf{u}_{in}}{m} > 0$. Hence, the errors \mathbf{e}_u converge asymptotically to $\mathbf{0}_{S_u}$ as $t \rightarrow \infty$ for any $\mathbf{e}_u(0)$. Thus, after

a long enough time, the estimated concentrations $\hat{\mathbf{c}}_u$ also converge towards the true concentrations \mathbf{c}_u .

E.2 Gas–liquid reaction systems

In G–L reaction systems, the mass-transfer rates are often unknown in addition to the reaction kinetics in the liquid phase. The number of moles \mathbf{n}_g in the gas phase can often be measured using gas analyzers at the gas outlet. Then, the extents of mass transfer in the gas phase can be computed from the number of moles measured in the gas phase under the assumption that the mass-transfer phenomena are described by the two-film theory with no accumulation in the boundary layer, as shown in Eq. (5.9c).

To design asymptotic observers, the following assumptions are introduced: (E5) the stoichiometric matrix \mathbf{N} , the inlet-composition matrices ($\mathbf{W}_{in,l}$ and $\mathbf{W}_{in,g}$), and the mass-transfer matrices ($\mathbf{W}_{m,l}$ and $\mathbf{W}_{m,g}$) are known; (E6) the $S_{g,a}$ concentrations in the gas phase ($\mathbf{c}_{g,a}$) and $S_{l,a}$ concentrations in the liquid phase ($\mathbf{c}_{l,a}$) are measured such that (i) $S_{l,a} + S_{g,a} \geq R + p_m$, (ii) $\mathbf{W}_{m_g,g} = p_{m_g}$, and (iii) $\text{rank}([\mathbf{N}_{l,a}^T, \mathbf{W}_{m_l,l,a}]) = R + p_{m_l}$; (E7) $\mathbf{u}_{in,l}$, $\mathbf{u}_{in,g}$, $u_{out,g}$, $u_{out,l}$, m_g , m_l and V_l are measured without errors; and (E8) estimates of the initial concentrations ($\hat{\mathbf{c}}_{l0}$ and $\hat{\mathbf{c}}_{l0}$) of species in the liquid and gas phases are available. The asymptotic observers in G–L reaction systems can then be designed as detailed in the following corollary:

Corollary E.1 (Asymptotic observers: G–L reaction systems)

For a G–L reaction system described by Eqs. (3.9)–(3.10) under Assumptions (A1)–(A4). If Assumptions (E5)–(E8) are also valid, then Eqs. (5.9a)–(5.11c) and the following equations

$$\hat{\mathbf{c}}_{l,u} = \frac{\mathbf{N}_u^T \hat{\mathbf{x}}_r + \mathbf{W}_{m_l,l,u} \hat{\mathbf{x}}_{m_l} + \mathbf{W}_{m_g,l,u} \hat{\mathbf{x}}_{m_g,l} + \mathbf{W}_{in,l,u} \hat{\mathbf{x}}_{in,l} + \hat{\lambda}_l \hat{\mathbf{n}}_{l0,u}}{V_l}, \quad (\text{E.8})$$

form an asymptotic observer for S_u unmeasured species in the liquid phase, where $\hat{\mathbf{c}}_{l,u}$ is the $S_{l,u}$ -dimensional vector of the estimated concentrations of unmeasured species. The vector of the estimation errors of the unmeasured concentrations, $\mathbf{e}_{l,u} = \mathbf{c}_{l,u} - \hat{\mathbf{c}}_{l,u}$, with $\mathbf{c}_{l,u}$ being the true concentrations of unmeasured species in the liquid phase, is given by

$$\mathbf{e}_{l,u} = (\mathbf{N}_u^T (\mathbf{x}_r - \hat{\mathbf{x}}_r) + \mathbf{W}_{m_l,l,u} (\mathbf{x}_{m_l} - \hat{\mathbf{x}}_{m_l}) + \mathbf{W}_{m_g,l,u} (\mathbf{x}_{m_g,l} - \hat{\mathbf{x}}_{m_g,l}) + \mathbf{W}_{in,l,u} (\mathbf{x}_{in,l} - \hat{\mathbf{x}}_{in,l}) + \lambda_l \mathbf{n}_{l0,u} - \hat{\lambda}_l \hat{\mathbf{n}}_{l0,u}) / V_l. \quad (\text{E.9})$$

If at least one of the inlet flowrates in the liquid phase is nonzero for a long enough time, then the estimated errors of the unmeasured concentrations are asymptotically stable and converge to zeros. (Proof follows from Proposition E.1)

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