Concept of Variants and Invariants for Reaction Systems, with Application to Estimation, Control and Optimization

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The only thing more expensive than education
is ignorance.
— Benjamin Franklin

To Laura
and my parents

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Abstract

The concept of reaction variants and invariants for lumped reaction systems has been known for several decades. Its applications encompass model identification, data reconciliation, state estimation and control using kinetic models. In this thesis, the concept of variants and invariants is extended to distributed reaction systems and used to develop new applications to estimation, control and optimization.

The thesis starts by reviewing the material and heat balances and the concept of variants and invariants for several lumped reaction systems. Different definitions of variants and invariants, in particular the vessel extents, are presented for the case of homogeneous reaction systems, and transformations to variants and invariants are obtained. The extension to systems with heat balance and mass transfer is also reviewed.

The concept of extents is generalized to distributed reaction systems, which include many processes involving reactions and described by partial differential equations. The concept of extents and the transformation to extents are detailed for various configurations of tubular reactors and reactive separation columns, as well as for a more generic framework that is independent of the configuration.

New developments of the extent-based incremental approach for model identification are presented. The approach, which compares experimental and modeled extents, results in maximum-likelihood parameter estimation if the experimental extents are uncorrelated and the modeled extents are unbiased. Furthermore, the identification problem can be reformulated as a convex optimization problem that is solved efficiently to global optimality.

The estimation of unknown rates without the knowledge or the identification of the rate models is described. This method exploits the fact that the variants computed from the available measurements allow isolating the different rates. Upon using a Savitzky-Golay filter for differentiation of variants, one can show that the resulting rate estimator is optimal and obtain the error and variance of the rate estimates.

The use of variants and invariants for reactor control is also considered. Firstly, offset-free control via feedback linearization is implemented using kinetic models. Then, it is shown how rate estimation can be used for control via feedback linearization without kinetic models. By designing an outer-loop feedback controller, the expected values of the

controlled variables converge exponentially to their setpoints.

This thesis presents an approach to speed up steady-state optimization, which takes advantage of rate estimation without rate models to speed up the estimation of steady state for imperfectly known dynamic systems with fast and slow states. Since one can use feedback control to speed up convergence of the fast part, rate estimation allows estimating the steady state of the slow part during transient operation.

The application to dynamic optimization is also shown. Adjoint-free optimal control laws are computed for all the types of arcs in the solution. In the case of reactors, the concept of extents allows the symbolic computation of optimal control laws in a systematic way. A parsimonious input parameterization is presented, which approximates the optimal inputs well with few parameters. For each arc sequence, the optimal parameter values are computed via numerical optimization.

The theoretical results are illustrated by simulated examples of reaction systems.

Keywords: Reaction systems, Variants, Invariants, Extents, Parameter estimation, Rate estimation, Control, Steady-state optimization, Dynamic optimization.

Résumé

Le concept de variants et d'invariants réactionnels pour les systèmes de réaction à paramètres localisés est connu depuis plusieurs décennies. Ses applications englobent l'identification de modèles, la réconciliation de données, l'estimation d'état et la commande basée sur des modèles cinétiques. Dans cette thèse, le concept de variants et d'invariants est étendu aux systèmes de réaction à paramètres distribués et est utilisé pour développer de nouvelles applications dans les domaines de l'estimation, de la commande et de l'optimisation.

La thèse commence par la révision des bilans de matière et d'énergie, et du concept de variants et d'invariants pour plusieurs systèmes de réaction à paramètres localisés. Différentes définitions de variants et d'invariants, en particulier celles des avancements généralisés, sont présentées dans le cas de systèmes réactionnels homogènes, et des transformations en variants et invariants sont données. L'extension aux systèmes avec un bilan d'énergie et un transfert de masse est également passée en revue.

Le concept d'avancement est généralisé aux systèmes de réaction à paramètres distribués, qui se retrouvent dans de nombreux procédés réactionnels décrits par des équations différentielles aux dérivées partielles. Le concept d'avancements et la transformation en avancements sont détaillés pour différentes configurations de réacteurs tubulaires et de colonnes de séparation réactive, ainsi que pour un cadre plus générique indépendant de la configuration.

De nouveaux développements de l'approche incrémentale basée sur les avancements pour l'identification de modèles sont présentés. L'approche, qui compare les avancements expérimentaux et modélisés, aboutit à une estimation des paramètres dans le sens d'un maximum de vraisemblance si les avancements expérimentaux ne sont pas corrélés et les avancements modélisés ne sont pas biaisés. De plus, le problème d'identification peut être reformulé comme un problème d'optimisation convexe qui est résolu efficacement dans le sens d'une optimalité globale.

L'estimation de vitesses inconnues sans la connaissance ou l'identification de modèles des vitesses est décrite. Cette méthode exploite le fait que les variants calculés à partir des mesures disponibles permettent d'isoler les différentes vitesses. En utilisant un filtre de Savitzky-Golay pour dériver les variants, on peut montrer que l'estimateur de vitesses

résultant est optimal et obtenir l'erreur et la variance associées à l'estimation de ces vitesses.

L'utilisation de variants et d'invariants pour la commande de réacteurs est également considérée. Premièrement, une commande sans erreur avec une linéarisation par rétroaction est mise en œuvre en utilisant des modèles cinétiques. Ensuite, il est montré comment l'estimation de vitesses peut être utilisée pour la commande avec linéarisation par rétroaction sans modèles cinétiques. En concevant un régulateur agissant par rétroaction dans la boucle externe, les valeurs attendues des variables contrôlées convergent exponentiellement vers leurs consignes.

Cette thèse présente une approche pour accélérer l'optimisation statique, qui tire parti de l'estimation de vitesses sans modèles de vitesses pour accélérer l'estimation de l'état stationnaire pour des systèmes dynamiques imparfaitement connus comprenant des états rapides et lents. Comme il est possible d'utiliser la commande par rétroaction pour accélérer la convergence vers l'état stationnaire de la partie rapide, l'estimation de vitesses permet d'estimer l'état stationnaire de la partie lente pendant le fonctionnement transitoire.

L'application à l'optimisation dynamique est aussi montrée. Les lois de commande optimale sans adjoints sont calculées pour tous les types d'arcs dans la solution. Dans le cas des réacteurs, le concept d'avancements permet le calcul symbolique de lois de commande optimale de manière systématique. Un paramétrage parcimonieux des entrées est présenté, qui approxime bien les entrées optimales avec peu de paramètres. Pour chaque séquence d'arcs, les valeurs optimales des paramètres sont calculées par optimisation numérique.

Les résultats théoriques sont illustrés par des exemples simulés de systèmes réactionnels.

Mots-clés : Systèmes réactionnels, Variants, Invariants, Avancements, Estimation de paramètres, Estimation de vitesses, Commande, Optimisation statique, Optimisation dynamique.

Contents

List of Figures

List of Tables

Nomenclature

Matrices are denoted by uppercase and boldface Latin, Greek or calligraphic symbols (except matrices of densities, which are denoted by lowercase and boldface Greek symbols). Vectors are denoted by lowercase and boldface Latin or Greek symbols (except vectors of enthalpies, which are denoted by uppercase and boldface Latin symbols). Scalars are denoted by italic Latin or lowercase and italic Greek symbols (except distances, which are denoted by uppercase calligraphic symbols). Sets, functionals, and functions of functions are denoted by uppercase Greek or calligraphic symbols. For each group of symbols, the following order is used: uppercase and boldface, lowercase and boldface, uppercase, lowercase.

Accents

$\bar{(\cdot)}$	average or steady-state quantity / reformulated function that uses or checks the necessary conditions of optimality
$\ddot{(\cdot)}$	second time derivative
$\dot{(\cdot)}$	first time derivative
$\hat{(\cdot)}$	modeled or reconciled quantity / estimate or estimator / terminal cost or constraint as a function of the decision variables
$\tilde{(\cdot)}$	experimental or measured quantity / extended state or function of extended states / scaled variable

Calligraphic symbols

$\mathscr{A}$	matrix that relates $\mathbf{r}_v$ to the available states $\mathbf{y}$ ($n_y \times R$)
$\mathscr{C}$	matrix that relates $\mathbf{u}_{in}$ to the available states $\mathbf{y}$ ($n_y \times p$)
$\mathscr{L}$	transformation matrix to original states or variables (for example, numbers of moles or related quantities)
$\mathscr{M}_j$	matrix used to compute an optimal control law for the input u_j ($\rho_j \times \rho_j$)
$\mathscr{T}$	transformation matrix to variants or extents
$\mathscr{A}$	set that contains the number of admissible standard deviations of the controlled variables
$\mathscr{C}$	compact set that contains the optimal parameters $\Delta\boldsymbol{\theta}$
$\mathscr{D}$	set of the spatial coordinates of a distributed reaction system

$\mathscr{E}$ set of conserved quantities

$\mathscr{E}_j$ auxiliary function defined recursively in terms of r and used to compute the estimators $\hat{r}^n$

$\mathscr{H}$ Hamiltonian function

$\mathscr{J}$ functional for the terminal cost as a function of the input trajectory and final time

$\mathscr{K}_n$ set of vectors of monomial powers of a polynomial of degree n

$\mathscr{L}$ Lagrangian function

$\mathscr{M}$ set of candidate models

$\mathscr{N}$ normal distribution

$\mathscr{O}$ functional for the terminal equality constraints as a function of the input trajectory and final time

$\mathscr{R}$ radius of tubular reactor

$\mathscr{S}$ set of species

$\mathscr{T}$ functional for the terminal inequality constraints as a function of the input trajectory and final time

$\mathscr{X}$ abstract species

Greek symbols

$\mathbf{\Gamma}$ diagonal matrix of desired exponential convergence rates for the controlled variables $\mathbf{x}$ (n_x-dim.)

$\mathbf{\Sigma}_{\tilde{\mathbf{y}}}$ variance-covariance matrix with respect to the measurements $\tilde{\mathbf{y}}$

$\boldsymbol{\alpha}$ vector of parameters appearing linearly in the reaction rate law (L-dim.)

$\boldsymbol{\beta}_a$ vector of zero-order part (with respect to the inputs $\mathbf{u}$) of the known dynamics of the fast or controlled states $\mathbf{x}$ (n_x-dim.)

$\boldsymbol{\chi}$ vector of spatial coordinates (3-dim.) / vector of concatenated terminal cost and constraints ($(n_\omega + n_\psi + 1)$-dim.)

$\boldsymbol{\eta}$ vector of Lagrange multipliers that correspond to $\mathbf{h}$ (n_h-dim.)

$\boldsymbol{\lambda}$ vector of adjoint variables that correspond to $\mathbf{x}$ (n_x-dim.)

$\boldsymbol{\mu}$ vector of means / vector of Lagrange multipliers that correspond to $\mathbf{g}$ (n_g-dim.)

$\boldsymbol{\nu}$ vector of Lagrange multipliers that correspond to $\boldsymbol{\psi}$ (n_ψ-dim.)

$\boldsymbol{\omega}$ vector of terminal equality constraints (n_ω-dim.)

$\boldsymbol{\phi}$ vector of rates that affect the numbers of moles (S-dim.)

$\boldsymbol{\phi}_d$ vector of molar diffusion rates (p_d-dim.)

$\boldsymbol{\phi}_{m,f}$ vector of molar rates of mass transfer to phase F ($p_{m,f}$-dim.)

$\boldsymbol{\varphi}$ vector of reaction rates in terms of numbers of moles or related quantities (R-dim.)

$\boldsymbol{\pi}$ vector of decision variables that represent inputs or setpoints (n_u-dim.) / vector of Lagrange multipliers that correspond to $\mathbf{h}$ at θ (n_h-dim.)

$\boldsymbol{\psi}$ vector of terminal inequality constraints (n_ψ-dim.)

$\boldsymbol{\rho}$	diagonal matrix of pure component densities (S-dim.)
τ	vector of decision variables of the dynamic optimization problem ($(n_s + 1 + n_z - n_x)$-dim.)
$\bar{\boldsymbol{\theta}}$	vector around which r as a function of $\boldsymbol{\theta}$ is represented as a Taylor series (N-dim.)
$\Delta\boldsymbol{\theta}$	vector of deviation of the parameters $\boldsymbol{\theta}$ around $\bar{\boldsymbol{\theta}}$ (N-dim.)
$\boldsymbol{\theta}$	vector of parameters appearing nonlinearly in the reaction rate law (N-dim.)
ξ	vector of Lagrange multipliers that correspond to $\boldsymbol{\omega}$ (n_ω-dim.)
ξ_{in}	vector of batch extents of inlet (p-dim.)
ξ_{iv}	vector of invariants (q-dim.)
ξ_r	vector of batch extents of reaction (R-dim.)
ζ	vector of adjoint variables that correspond to $\mathbf{z}$ (n_z-dim.)
ζ_i	vector of adjoint variables that correspond to $\mathbf{z}_i$ ($n_{z,i}$-dim.)
Φ	set of admissible trajectories of the available rates
Ψ	set of admissible trajectories of the available states
Θ	set of possible parameters of a model
α	number of a conserved quantity in a species / inverse of the time constant of the dynamic relationship between $\mathbf{x}^s$ and their steady state / relative volatility
β_q/γ_q	auxiliary functions used to compute the covariance of the differentiation Savitzky-Golay filter
χ	terminal cost or constraint
ϵ	small parameter
ε_f	volumetric fraction of phase F
γ	weights that specify a numerical quadrature method
ν	stoichiometric coefficient
ω	inverse of the residence time
$\dot{\phi}$	angular speed of the stirrer
ϕ	objective function / terminal cost
π_i	number of pieces of the cubic splines in the ith time interval
ψ	rates that affect the heat
ρ	density
ρ_j	number of states $\mathbf{x}^{u_j}$
σ	standard deviation
τ	fast time scale
θ	entry point of a constraint $\mathbf{h}$
υ	volume in terms of numbers of moles or related quantities
$\xi_{j,i}$	degree for which there is an optimal control law for the input u_j in the ith time interval
ζ	cost of the convex optimization problem for estimation of parameters $\Delta\boldsymbol{\theta}$

Latin symbols

$\mathbf{0}$	vector or matrix of appropriate dimension with all elements being 0

$\mathbf{1}$	vector or matrix of appropriate dimension with all elements being 1
$\mathbf{A}$	atomic matrix ($S \times E_d$) / state matrix of the linearized system
$\mathbf{B}$	input matrix of the linearized system
$\mathbf{B}_a$	matrix of first-order part (with respect to the inputs $\mathbf{u}$) of the known dynamics of the fast or controlled states $\mathbf{x}$ ($n_x \times n_x$)
$\mathbf{C}_{cal}$	matrix of calibration concentrations ($H \times S$)
$\mathbf{C}_x/\mathbf{C}_z$	output matrix for the available outputs $\mathbf{y}$ as a function of the fast states $\mathbf{x}$ ($n_y \times n_x$) / slow states $\mathbf{z}$ ($n_y \times n_z$)
$\mathbf{D}$	diagonal matrix of desired reduction of the time constants of the actuators (n_x-dim.)
$\mathbf{E}_d$	diffusion matrix ($S \times p_d$)
$\mathbf{E}_{m,f}$	mass-transfer matrix for phase F ($S_f \times p_{m,f}$)
$\mathbf{F}$	matrix that relates $\mathbf{r}_u$ to the fast or controlled states $\mathbf{x}$ ($n_x \times n_r$)
$\Delta\mathbf{H}$	vector of enthalpies of formation (S-dim.)
$\Delta\mathbf{H}_d$	vector of enthalpies of diffusion (p_d-dim.)
$\Delta\mathbf{H}_{m,f}$	vector of enthalpies of mass transfer to phase F ($p_{m,f}$-dim.)
$\Delta\mathbf{H}_r$	vector of enthalpies of reaction (R-dim.)
$\Delta^T\mathbf{H}_r$	vector of enthalpies of reaction at the reactor temperature (R-dim.)
$\mathbf{H}$	Hessian or second-order matrix / matrix that relates $\mathbf{r}_u$ to the slow states $\mathbf{z}$ ($n_z \times n_r$)
$\mathbf{H}_a$	matrix that specifies a linear relationship between the slow states $\mathbf{z}$ and the available rates $\mathbf{h}_a$ ($n_z \times n_z$)
$\mathbf{H}_m$	vector of molar enthalpies (S-dim.)
$\mathbf{I}$	identity matrix of appropriate dimension
$\mathbf{J}_{d,f}$	matrix of diffusion fluxes in phase F ($p_d \times 3$)
$\mathbf{K}$	diagonal matrix of control gains
$\mathbf{L}$	matrix of linear combinations
$\mathbf{M}_w$	diagonal matrix of pure component molecular weights (S-dim.)
$\mathbf{N}$	stoichiometric matrix ($R \times S$)
$\mathbf{P}$	transformation matrix to invariants ($S \times q$)
$\mathbf{Q}_b$	positive semidefinite matrix related to the vector $\mathbf{v}_{d-b}$
$\mathbf{Q}_n/\mathbf{Q}_x$	matrix of first-order part of the relation between inputs of the linearized reaction system in terms of $\mathbf{n}_a$ / $\mathbf{x}_v$ ($n_u \times n_u$)
$\mathbf{R}$	matrix of reaction rates
$\mathbf{R}_{b,\mathbf{k}}$	localizing matrix related to the monomial with powers $\mathbf{k}$ of the vector $\mathbf{v}_{d-b}$
$\mathbf{S}$	matrix of molar sensitivities ($S \times W$)
$\mathbf{S}_n/\mathbf{S}_x$	selection matrix for the reaction system in terms of $\mathbf{n}_a$ / $\mathbf{x}_v$

$\check{\mathbf{T}}_{in}$	vector of inlet specific heats (p-dim.)
$\mathbf{T}_a$	diagonal matrix of time constants of the actuators (n_u-dim.)
$\mathbf{T}_i$	diagonal matrix of integral times
$\mathbf{U}_a$	inverse matrix of $\mathbf{B}_a$ ($n_x \times n_x$)
$\mathbf{V}_{pr}$	prognostic matrix ($S \times W$)
$\mathbf{W}$	weighting matrix
$\mathbf{W}_{in}$	inlet-composition matrix ($S \times p$)
$\mathbf{Y}_{cal}$	matrix of calibration measurements ($H \times W$)
$\mathbf{Z}_{in,h}$	matrix of molar fractions of the liquid inlets at the hth intermediate inlet/outlet ($S_l \times p_{l,h}$), or to the nth tray ($S_l \times p_{l,n}$) if h is replaced by n
$\mathbf{b}$	vector that relates q_{ex} to the available states $\mathbf{y}$ (n_y-dim.)
$\mathbf{b}_n/\mathbf{b}_x$	vector of implicit variables of the linearized reaction system in terms of $\mathbf{n}_a$ / $\mathbf{x}_v$ ($(R+1)$-dim.)
$\mathbf{c}$	vector of concentrations (S-dim.)
$\mathbf{c}_p$	vector of molar heat capacities at constant pressure (S-dim.)
$\delta\mathbf{c}$	vector of quantities related to concentrations (S-dim.)
$\mathbf{d}_\mathbf{y}$	vector of noise variables with respect to the measurements of $\mathbf{y}$
$\mathbf{e}$	vector of control errors (n_x-dim.)
$\mathbf{e}_i$	unit vector of the standard basis related to the ith reaction (R_i-dim.)
$\check{\mathbf{f}}_j$	vector of dynamics of all the states $\mathbf{x}$ except x_j ((n_x-1)-dim.)
$\mathbf{f}$	vector of dynamics of the fast or controlled states $\mathbf{x}$ (n_x-dim.)
$\mathbf{f}^{\mu_j}$	vector of dynamics of $\mathbf{x}^{\mu_j}$ (ρ_j-dim.)
$\mathbf{f}_{in,h}$	vector of molar flowrates of the liquid inlets at the hth intermediate inlet/outlet ($p_{l,h}$-dim.), or to the nth tray ($p_{l,n}$-dim.) if h is replaced by n
$\tilde{\mathbf{f}}$	vector of dynamics of the extended states $\mathbf{z}$ (n_z-dim.)
$\mathbf{g}$	gradient or first-order vector / vector of inequality or mixed path constraints (n_g-dim.)
$\Delta^T\mathbf{h}_{in}$	vector of specific enthalpies of the inlets with respect to the reactor (p-dim.)
$\mathbf{h}$	vector of dynamics of the slow states $\mathbf{z}$ (n_z-dim.) / vector of pure-state path constraints (n_h-dim.)
$\mathbf{h}_{in}$	vector of specific enthalpies of the inlets (p-dim.)
$\mathbf{j}_{d,z}$	vector of diffusion fluxes in the z-direction (p_d-dim.)
$\mathbf{k}$	vector of monomial powers of a Taylor series (N-dim.)
$\mathbf{k}_{in}$	vector that specifies a linear relationship between $\mathbf{u}_{in}$ and ω (p-dim.)
$\mathbf{k}_r$	vector that specifies a linear relationship between $\mathbf{r}_v$ and ω (R-dim.)

$\delta\mathbf{n}$	vector of quantities related to number of moles (S-dim.)
$\mathbf{n}$	vector of number of moles (S-dim.)
$\mathbf{n}_0$	vector of initial numbers of moles (S-dim.)
$\mathbf{n}_a$	vector of numbers of moles with the minimal size needed to describe the reaction system (($R+p$)-dim.)
$\mathbf{n}_o$	vector of numbers of moles in $\mathbf{n}_a$ with relative degree one with respect to $\mathbf{u}_{in}$ (p-dim.)
$\mathbf{n}_t$	vector of numbers of moles in $\mathbf{n}_a$ with relative degree two with respect to $\mathbf{u}_{in}$ (R-dim.)
$\vec{\mathbf{n}}$	inward-pointing normal vector (3-dim.)
$\mathbf{p}_{j,i}$	vector of parameters of the cubic spline that describes the input u_j in the ith time interval ($b_{j,i}\pi_i$-dim.)
$\mathbf{p}_n/\mathbf{p}_x$	vector of zero-order part of the relation between inputs of the linearized reaction system in terms of $\mathbf{n}_a$ / $\mathbf{x}_v$ (n_u-dim.)
$\mathbf{q}_i$	vector of dynamics of $\mathbf{z}_i$ ($n_{z,i}$-dim.)
$\mathbf{r}$	vector of reaction rates (R-dim.)
$\mathbf{r}_u$	vector of unknown rates (n_r-dim.)
$\mathbf{r}_v$	vector of reaction rates in $\frac{\text{moles}}{\text{time}}$ (R-dim.)
$\mathbf{s}$	vector of functions that compute an estimate of the steady state of the slow states $\mathbf{z}$ (n_z-dim.)
$\mathbf{s}_a$	vector of available rates (n_y-dim.)
$\mathbf{s}_r/\mathbf{s}_t$	vector of rates that represent the derivative of $\mathbf{x}_r$ / $\mathbf{n}_t$ (R-dim.)
$\mathbf{s}_u$	vector of unknown dynamics of the fast or controlled states $\mathbf{x}$ that does not depend on $\mathbf{r}_u$ (n_x-dim.)
$\mathbf{t}_n/\mathbf{t}_x$	vector of transformation to the variables $\mathbf{z}_n/\mathbf{z}_x$ of the linearized reaction system (($R+n_u$)-dim.)
$\mathbf{t}_n^{-1}/\mathbf{t}_x^{-1}$	vector of inverse transformation from the variables $\mathbf{z}_n/\mathbf{z}_x$ of the linearized reaction system (($R+n_u$)-dim.)
$\mathbf{t}_{r,i}$	transformation vector from measured quantities to the ith experimental extent of reaction (W_i-dim.)
$\bar{\mathbf{u}}$	vector of actuator inputs (n_u-dim.)
$\delta\mathbf{u}$	vector of deviation variables related to the inputs $\mathbf{u}$ (n_u-dim.)
$\mathbf{u}$	vector of inputs (n_u-dim.)
$\mathbf{u}_{in}$	vector of inlet mass/volumetric flowrates (p-dim.)
$\mathbf{v}$	vector of new inputs of the linearized system
$\mathbf{v}_d$	vector of monomials up to degree d in the N variables $\Delta\boldsymbol{\theta}$ ($s(N,d)$-dim.)
$\mathbf{v}_f$	vector of advective velocities in phase F (3-dim.)
$\mathbf{v}_m$	vector of molar volumes (S-dim.)
$\mathbf{v}_n/\mathbf{v}_x$	vector of new inputs of the linearized reaction system in terms of $\mathbf{n}_a$ / $\mathbf{x}_v$ (n_u-dim.)

$\check{\mathbf{w}}_{in,j}$	vector of weight fractions of the jth inlet (S-dim.)
$\mathbf{w}$	vector of zero-order part (with respect to the inputs $\mathbf{u}$) of the dynamics of the fast or controlled states $\mathbf{x}$ (n_x-dim.)
$\mathbf{w}_{in}$	vector of volumetric extents of inlet (p-dim.)
$\mathbf{w}_{iv}$	vector of invariants (q-dim.)
$\mathbf{w}_r$	vector of volumetric extents of reaction (R-dim.)
$\check{\mathbf{x}}_j$	vector of all the states $\mathbf{x}$ except x_j (($n_x - 1$)-dim.)
$\delta\mathbf{x}$	vector of deviation variables related to the fast or controlled states $\mathbf{x}$ (n_x-dim.)
$\mathbf{x}$	vector of fast or controlled states (n_x-dim.)
$\mathbf{x}^{u_j}$	vector of states that are reachable by manipulating the input u_j (ρ_j-dim.)
$\mathbf{x}_c$	vector of subset of the fast states with the same dimension as the inputs $\mathbf{u}$ (n_u-dim.)
$\mathbf{x}_d$	vector of extents of diffusion (p_d-dim.)
$\mathbf{x}_{in}$	vector of (vessel) extents of inlet (p-dim.)
$\mathbf{x}_{iv}$	vector of invariants (q-dim.)
$\mathbf{x}_{m,f}$	vector of (vessel) extents of mass transfer to phase F ($p_{m,f}$-dim.)
$\mathbf{x}_r$	vector of (vessel) extents of reaction (R-dim.)
$\mathbf{x}_v$	vector of vessel extents (($R + p$)-dim.)
$\mathbf{y}$	vector of measured quantities (W-dim.) / vector of available states or outputs (n_y-dim.)
$\mathbf{y}_{iv}$	vector of reaction invariants (q-dim.)
$\mathbf{y}_r$	vector of reaction variants (R-dim.) / vector of variants with respect to unknown rates (n_r-dim.)
$\mathbf{z}$	vector of numbers of moles and heat, or concentrations and temperature (($S + 1$)-dim.) / vector of slow states, or extended states (n_z-dim.)
$\mathbf{z}_{in}$	vector of inlet variants and reaction invariants (p-dim.)
$\mathbf{z}_{iv}$	vector of reaction and inlet invariants (q-dim.)
$\mathbf{z}_i$	vector of extended states in the ith time interval ($n_{z,i}$-dim.)
$\mathbf{z}_n/\mathbf{z}_x$	vector of new states of the linearized reaction system in terms of $\mathbf{n}_a$ / $\mathbf{x}_v$ (($R + n_u$)-dim.)
$\mathbf{z}_r$	vector of reaction variants and inlet invariants (R-dim.)
A	heat transfer area / cross-section area of reactive separation column
B	molar amount in the bottoms tank
D	number of percentiles for discretization of the distribution / molar amount in the distillate tank
E	number of conserved quantities

$E_{a,i}$	activation energy of the ith reaction
F	cumulative distribution function of a normally distributed random variable
F^{-1}	inverse distribution function of a normally distributed random variable
F_s	volumetric flowrate of an inlet stream for species s
G	molar advective flowrate of the gas phase
H	enthalpy / number of samples
J	cost function
L	molar advective flowrate of the liquid phase / number of parameters $\boldsymbol{\alpha}$
M	stirrer torque / molar holdup in the liquid phase on a tray
N	number of trays / number of parameters $\boldsymbol{\theta}$
P	pressure
P_a/P_b	polynomial in the denominator / numerator of the cost function for estimation of parameters $\Delta\boldsymbol{\theta}$
$P_{in,j}$	pressure of the jth inlet
Q	heat
R	number of independent reactions / ideal gas constant
S	number of species
ΔT_j	difference between the temperatures of the inlet and the outlet of the jacket
T	temperature of the reaction mixture
$T_{in,j}$	temperature of the jth inlet
T_j	jacket temperature
U	overall heat transfer coefficient
V	volume of the reaction mixture / molar advective flowrate of the vapor phase
V_t	total volume
W	number of measured quantities $\mathbf{y}$
Z	normally distributed random variable
$a_\mathbf{k}/b_\mathbf{k}$	coefficient of the polynomial P_a / P_b
$b_{j,i}$	binary constant that specifies if $\mathbf{p}_{j,i}$ exists or not
b_k/c_k	kth convolution coefficient of the averaging filter / differentiation filter
c	constant or zero-order scalar
$c_{in,s}$	concentration of species s in an inlet stream for that species
c_j	optimal control law for the jth input
c_p	specific heat capacity
d	degree of the polynomials in the convex optimization problem for estimation of parameters $\Delta\boldsymbol{\theta}$
d_ℓ	weighted integral of the rate r_ℓ
h	sampling period
k_i	rate constant of the ith reaction
m	mass of the reaction mixture

$\tilde{n}_i$	number of switching times to arcs specified by pure-state path constraints in the ith time interval
n	degree of the reaction rate represented as a Taylor series
n_ω	number of terminal equality constraints $\boldsymbol{\omega}$
n_ψ	number of terminal inequality constraints $\boldsymbol{\psi}$
n_g	number of mixed path constraints $\mathbf{g}$
$n_{h,l}/n_{h,n}$	molar holdup in the liquid phase per unit length / of the nth tray
n_h	number of pure-state path constraints $\mathbf{h}$
n_r	number of unknown rates $\mathbf{r}_u$
n_s	number of switching times considered as decision variables
n_u	number of inputs $\mathbf{u}$
n_x	number of fast or controlled states $\mathbf{x}$
n_y	number of available states or outputs $\mathbf{y}$ and available rates $\mathbf{s}_a$
$n_{z,i}$	number of extended states $\mathbf{z}_i$
n_z	number of slow states $\mathbf{z}$ or extended states $\mathbf{z}$
p	number of independent inlets
p_d	number of diffusing species
$p_{l,h}$	number of independent inlets at the hth intermediate inlet/outlet, or to the nth tray if h is replaced by n
$p_{m,f}$	number of mass transfers to phase F
p_s	partial pressure of species s
q	number of invariants / number of samples used by the differentiation Savitzky-Golay filter
$q_{ex,rem}$	heat power that is not exchanged with the jacket (exchanged with the remaining environment)
q_{ex}	exchanged heat power
q_l	volumetric flowrate in the column
q_{out}	outlet volumetric flowrate
q_{rx}	heat power produced by the reactions
$\hat{r}^n$	nth-order estimator of r
r	radial coordinate / reaction rate candidate / reflux ratio
r_j	number of time differentiations of $\det(\mathscr{M}_j)$ needed to compute an optimal control law for u_j
$s(N,d)$	number of monomials up to degree d in N variables
Δt	length of the time window used by the differentiation Savitzky-Golay filter
t	time
t_f	final time
t_i^m	mth intermediate time instant of the cubic spline defined in the ith time interval between t_i^0 and $t_i^{\pi_i}$
t_{up}	upper bound for the final time
u_j	inlet flowrate of the jacket / jth input
u_{out}	outlet mass flowrate

v_z advective velocity in the axial direction

w_{ic} volumetric extent of initial conditions

w_i^m constant that specifies the position of t_i^m with respect to t_i^0 and $t_i^{\pi_i}$

x_{ex} (vessel) extent of heat exchange

x_{ic} (vessel) extent of initial conditions

x_j state with dynamics affected by the jth input

x_r (vessel) extent of reaction related to the rate candidate r

x_s mole fraction of species s in the liquid phase

y_s mole fraction of species s in the gas/vapor phase

z axial coordinate

Matrix and vector operators

$(\cdot)^+$ Moore-Penrose pseudoinverse of the matrix $(\cdot)$

$(\cdot)^{-1}$ inverse of the matrix $(\cdot)$

$(\cdot)^{\mathrm{T}}$ transpose of the matrix $(\cdot)$

$\Delta_j^l(\cdot)$ lth-order differentiator of the vector $(\cdot)$ with respect to the input u_j

$\det(\cdot)$ determinant of the matrix $(\cdot)$

$\mathrm{diag}(\cdot)$ diagonal elements of the matrix $(\cdot)$ / diagonal matrix with diagonal elements from the vector $(\cdot)$

$\| (\cdot) \|_p$ p-norm of the vector or matrix $(\cdot)$

$\mathrm{rank}(\cdot)$ rank of the matrix $(\cdot)$

$\mathrm{tr}(\cdot)$ trace of the matrix $(\cdot)$

Other operators

$\mathscr{D}_q(\cdot, t)$ differentiation Savitzky-Golay filter of order 1 and window size q applied to the function $(\cdot)$ on an interval that ends at t

$\mathscr{R}_q(\cdot, t)$ remainder term applied to the function $(\cdot)$ on an interval that ends at t, related to the filter $\mathscr{D}_q$

$\mathscr{W}_q(\cdot, t)$ weighted average filter applied to the function $(\cdot)$ on an interval that ends at t, related to the filter $\mathscr{D}_q$

$\nabla(\cdot)$ gradient or spatial derivative of the function $(\cdot)$

$\mathrm{B}_{\hat{r}}(\cdot)$ bias associated with the estimator $\hat{r}$ given that the argument of $\hat{r}$ has expected value $(\cdot)$

$\mathrm{E}[\cdot]$ expected value of $[\cdot]$

$\mathrm{P}[\cdot]$ probability of $[\cdot]$

$\mathrm{Var}[\cdot]$ variance of $[\cdot]$

$\mathrm{int}(\cdot)$ interior of the set $(\cdot)$

$\partial(\cdot)$ boundary of the set $(\cdot)$

Subscripts

k running index for the vectors of monomial powers of a Taylor series

0 related to initial conditions or pre-exponential factors

B related to the bottoms tank

D related to the distillate tank

F related to fed species

I related to reactants that are not fed

N	related to stoichiometries
P	related to products
R	related to reactants
T	related to the total amount of all species
a	related to available or known quantities or functions, or a minimal set of variables needed to describe the reaction system
c	related to a convex reformulation or controlled variables
cal	related to calibration quantities
d	related to diffusion or linear dependence
e	running index for the conserved quantities / related to reactions with instantaneous equilibrium
ex	related to heat exchange
f	related to phase F or the final time
h	running index for the positions of intermediate inlets/outlets
i	running index for the reactions, or the time intervals and switching times
ibc	related to initial and boundary conditions
ic	related to initial conditions
iic	related to initial and inlet flow conditions
in	related to inlet flow
iv	related to invariants
j	running index for the inlets, the diffusing species, or the inputs / related to the jacket
k	running index for the mass transfers, the coefficients of the differentiation filter, the number of reached steady states, or the path constraints
ℓ	running index for the functions that compose a reaction rate law
l	related to liquid phase
m	running index for the time instants / related to mass, mass transfer or molar quantities
max	maximum value
min	minimum value
n	related to the nth tray, non-controlled variables, or numbers of moles
o	related to variables with relative degree one, or variables in the outer loop of a cascade control scheme
out	related to outlet flow
r	related to reactions, reactor, or the r-direction
r_i	running index for the subintervals in the ith time interval
ref	related to reference conditions
s	running index for the species / related to slow reactions
t	related to variables with relative degree two
u	related to unavailable or unknown quantities or functions

v	related to extensive quantities in the vessel
w	running index for the measured quantities
x	related to vessel extents
z	related to the z-direction

Superscripts

$*$	optimal value / vapor pressure
$+$	produced
$-$	consumed
ε	multiplied by the volumetric fraction of the phase
m	related to the mth intermediate time instant of the cubic spline
$n/(n)$	nth time derivative
RFV	reaction-flow-variant form
RV	reaction-variant form
UV	unknown-variant form
s	setpoint
u_j	related to the jth input
v	multiplied by the volume of the phase
$vRFV$	vessel reaction-flow-variant form
vRV	vessel reaction-variant form

1 Introduction

Part of this chapter is adapted from the postprint of the following article [1]:

D. Rodrigues, S. Srinivasan, J. Billeter, and D. Bonvin. Variant and invariant states for chemical reaction systems. *Comput. Chem. Eng.*, 73:23–33, 2015.

Link: http://doi.org/10.1016/j.compchemeng.2014.10.009.

The author of this thesis contributed to that article by developing the main novel ideas and writing a significant part of the text. Hence, the author retains the right to include the article in this thesis since it is not published commercially and the journal is referenced as the original source.

1.1 Motivation

Reaction systems are used by the process industry to convert raw materials into desired products. In particular, the (bio)chemical industry generates products that include polymers, organic chemicals, vitamins, vaccines and drugs. These processes not only involve chemical reactions, but also deal with (i) material exchange via inlet/outlet flows, mass transfers, convection, diffusion, and (ii) energy exchange via heating and cooling.

The models of the phenomena in these processes that involve reactions can be used for several different tasks that improve their understanding, design and operational performance. Three applications can be highlighted: (i) estimation, whereby various quantities that characterize the process, such as its states or parameters, are estimated for monitoring, prediction, diagnosis or use by other applications; (ii), control, which enforces operation of the process in a safe and reliable manner and ensures product quality; and (iii) optimization, which provides decision policies that use the available economic, human and environmental resources in the most efficient way, while fulfilling the requirements for a controlled and feasible process operation [2, 3, 4].

Models of (bio)chemical reaction processes may be empirical in nature [5], but they are typically first-principles models that describe the state evolution (the mass, the concentra-

tions, the temperature) by means of balance equations of differential nature (e.g. continuity equation, molar balances, heat balances) and constitutive equations of algebraic nature (e.g. equilibrium relationships, rate expressions) [6]. These models usually include information regarding the underlying reactions (e.g. stoichiometries, reaction kinetics, enthalpies of reaction), the transfers of mass within and between phases, and the operating mode of the reactor (e.g. initial conditions, external exchange terms, operating constraints).

The construction of these models, as well as their use during the process operation, relies on the collection of experimental data both in the laboratory and during production [7]. These experimental data can be obtained from a range of process measurements, such as temperature, pressure, pH, flow rate, chromatography, and calorimetric and spectroscopic (mid-infrared, near-infrared and ultraviolet/visible) measurements. Unfortunately, these measurements are typically corrupted by random measurement noise. Furthermore, since a reliable description of reaction kinetics and transport phenomena represents the main challenge in building first-principles models for reaction systems, this kinetic part of the model can be more or less detailed, and can be subject to more or less error. Hence, the modeling methods, the applications of models to operation, and their use of experimental data should fulfill their task in a way that reduces the detrimental effect on the process performance of errors and incompleteness in models and measurements [8].

The presence of all the physical phenomena, and in particular their interactions, complicates the analysis and operation of reaction systems. The analysis would be much simpler if one could somehow decouple the effect of the various phenomena and investigate each phenomenon individually. Furthermore, some of the states in a model are often redundant, as there are typically more states (balance equations) than there are independent sources of variability (reactions, exchange terms). Consequently, in this thesis, the general objective is to obtain representations of reaction systems that address these issues and allow the development of new methods that improve estimation, control and optimization for reaction systems.

1.2 State of the Art

As a result of the motivating remarks above, one would ideally like to have a systematic way of obtaining a system representation with (i) true variants, whereby each variant depends only on one phenomenon, and (ii) invariants that express redundancies and can be discarded, thereby reducing the dimensionality of the model. Although these concepts of variants and invariants are well-known and straightforward for batch reaction systems, it would be beneficial to generalize these concepts and their application to other reaction systems. Let us summarize the previous and current efforts to obtain such a system representation and to develop applications of this representation to improved analysis, design, and operation of reaction systems.

Aris and Mah [9] were among the first authors to discuss the use of the knowledge of the stoichiometric matrix for model reduction using the concept of extents. Fjeld, Asb-

jørnsen and co-workers [10, 12, 11, 13] introduced the concepts of reaction variants and reaction invariants and used them for modeling and control of continuous-stirred tank reactors. However, some of the reaction variants proposed in the literature encompass more than the reaction contributions since they are also affected by the inlet and outlet flows. Hence, Friedly [14, 15] proposed to compute the extents of equivalent batch reactions for open heterogeneous reactors, associating the remainder to transport processes, while Friedly and Rubin [16] provided linear transformations between concentrations and these reaction variants and invariants. For open homogeneous reaction systems, Srinivasan et al. [17] developed a nonlinear transformation of the numbers of moles to reaction variants, flow variants, and reaction and flow invariants, thereby separating the effects of reactions and flows. Later, Amrhein et al. [18] refined that transformation to make it linear (at the price of losing the one-to-one property) and therefore more easily interpretable and applicable. They also showed that, for a reactor with an outlet flow, the concept of vessel extent is most useful, as it represents the amount of material associated with a given process (reaction, exchange) that is still in the vessel. Bhatt et al. [19] extended that concept to heterogeneous gas-liquid reaction systems for the case of no reaction and no accumulation in the film, the result being decoupled vessel extents of reaction, mass transfer, inlet and outlet, as well as true invariants that are identically equal to zero.

In particular, the concept of extent of reaction is very useful to describe the dynamic behavior of a chemical reaction since a reaction rate is simply the derivative of the corresponding extent of reaction. Bonvin and Rippin [20] and Amrhein et al. [21] used batch extents of reaction to identify the stoichiometric matrix and the number of independent reactions without the knowledge of reaction kinetics via target factor analysis. The use of extents instead of concentrations for multivariate calibration has also been proposed to reduce the number of required calibration samples and to increase the signal-to-noise ratio [22, 23]. Owing to the concept of extents of reaction, the concentrations of all species can be reconstructed without knowledge of kinetics when there are at least as many measured species as independent reactions and the inlet and outlet flows are known [24, 23].

The connection between stoichiometric and atomic matrices and balances for species and elements has been investigated by Schneider and Reklaitis [25], and this analysis has been related with the concept of reaction invariants by Madron and Veverka [26]. The use of knowledge about the stoichiometry to detect structural invariants in biological reaction networks has also been documented [27].

Various implications of reaction variants/invariants have been studied in the literature. For example, Srinivasan et al. [17] discussed the implications of reaction and flow variants/invariants for control-related tasks such as model reduction, state accessibility, state reconstruction and feedback linearizability. On the one hand, control laws using reaction variants have been proposed for continuous stirred-tank reactors [28, 29, 30, 31, 32], in most cases using the kinetic model. In addition, Amrhein et al. [33] have shown that pretreating the calibration data and the spectral data to reaction-variant form is needed to ensure correct prediction of the concentrations of the spectral data when reacting mixtures

are used to generate the calibration data. Furthermore, the use of spectral data in reaction-variant form for multivariate curve resolution [34, 35] avoids rank deficiency of the spectral measurement matrix and eliminates the need to use rank augmentation techniques [36].

On the other hand, the fact that reaction invariants are independent of reaction progress has also been exploited for process analysis, design and control. For example, reaction invariants have been used to study the state controllability and observability of continuous stirred-tank reactors [13, 37]. The concept of reaction invariants has also been instrumental for the design of the so-called asymptotic observers [38, 39]. Furthermore, Waller and Mäkilä [29] and Gustafsson and Waller [40] demonstrated the use of reaction invariants to control pH, assuming that the equilibrium reactions are very fast. Aggarwal et al. [41] considered multi-phase reactors operating at thermodynamic equilibrium and were able to use the concept of reaction invariants, which they labeled invariant inventories, to reduce the order of the dynamic model and use it for control. A systematic method to determine reaction invariants has been presented and used to automate the task of formulating mole balance equations for the non-reacting part (such as mixing and splitting operations) of complex processes, thereby helping determine the number of degrees of freedom for process synthesis [42, 43].

The versatility of the concept of reaction invariants has been shown by its use in many different contexts, such as observer design for fuel cells [44] and efficiency computation for complex chemical systems with power production [45], and also to reduce the number of differential equations that describe the dynamic model of batch activated sludge processes [46]. Schultz et al. [47] defined reaction invariants in the context of carrier-mediated transport in membranes and used this concept to simplify the analysis of the transport. Barbosa and Doherty [48], and later Ung and Doherty [49], developed a nonlinear transformation to reaction-invariant compositions in reactive distillation columns to reduce the number of degrees of freedom in process design. This transformation to reaction invariants was later applied to reactive chromatography and membrane reactors [50], showing that the dynamic behavior of these reaction-separation processes with fast (equilibrium) reactions resembles the dynamic behavior of corresponding non-reactive systems in a reduced set of transformed variables. An important question regarding the correct choice of reference components required by this transformation has also been addressed [51, 52].

One of the main applications of the concept of variants and invariants is model reduction. In reaction systems that exhibit time-scale separation owing to the presence of fast and slow reactions, it has been shown that the slow dynamics are described by a lower-dimensional state space that is invariant with respect to the fast reactions [53]. In continuous stirred-tank reactors with multi-step biochemical reaction schemes, it was shown how the computation of reaction invariants allows neglecting the dynamics of the fast steps [54]. The use of invariants in model reduction for thin-film deposition systems has also been proposed [55]. Furthermore, the model reduction provided by the concept of extents has been useful to compute insightful optimal control laws for reaction systems with one or two reactions [56, 57].

Identification problems are commonly solved in one step using a simultaneous method, where an overall kinetic model comprising rate expressions for all dynamic effects is identified. This method suffers from combinatorial complexity and can lead to convergence problems and high parameter correlation [58]. As an alternative, the incremental methods break down the original identification problem into a set of subproblems of lower complexity, which allows the individual modeling of each dynamic effect. Incremental model identification is performed by comparing the rates or extents computed from measured concentrations to the values predicted by the model [59]. This comparison can be done individually for each reaction. This way, several rate expressions can be compared to experimental data, one at a time, until the correct expression has been found and the corresponding parameters identified. The incremental methods exist in two variants, (i) the rate-based approach that relies on a differential method of parameter estimation via rates [60, 61], and (ii) the extent-based approach that uses an integral method of parameter estimation via extents [18, 19]. Both the rate-based and the extent-based approach have been used for parameter estimation in biological network models [62, 63]. The route over extents has certain advantages, in particular in the presence of noisy and scarce measurements [58].

Incremental model identification in its extent-based form has been applied to open homogeneous and gas-liquid reaction systems and consists of two steps: first, measured concentrations are transformed into individual contributions of each dynamic effect, the extents; in a second step, the rate expressions are identified one at a time and the corresponding rate parameters are estimated [64]. Reaction extents have been used extensively for the kinetic identification of reaction systems using either concentration [58] or spectroscopic [23] measurements. An extension regarding the incorporation of calorimetric measurements into the extent-based identification framework has been proposed [65]. The extent-based approach has also been used for identification of multiphase reaction systems with instantaneous equilibria [66]. Regarding the implementation aspects, it has been claimed recently that the use of the adjoint method can speed up the computation of gradients for both the simultaneous and incremental approaches, in the context of kinetic identification of plug-flow reactors and continuous stirred-tank reactors [67, 68].

Other applications of variants and invariants, in particular of extents, have been developed. The existence of invariants allows one to derive invariant relationships among measured variables from the material and energy balances, which by itself allows the use of data reconciliation techniques [69]. Moreover, the rate decoupling provided by the extents, where each state is related to a single rate process, increases the likelihood of identifying constraints on the shape of the extents, such as monotonicity and curvature. Both the invariant relationships and the shape constraints have been used to improve data reconciliation and state estimation in reaction systems [70, 71], in the latter case via the use of a receding-horizon nonlinear Kalman filter that allows enforcing shape constraints during the update procedure. In the context of multivariate curve resolution via alternating regression, the use of the shape constraints and invariant relationships has also been shown to be advantageous to improve the signal-to-noise ratio in the concentration estimates [35]. Invariant relation-

ships derived from the element balances have been proposed recently as a way to reduce the number of feasible reactions in the inference of chemical reaction networks [72]. Furthermore, the invariant relationships have been used to compute reachable sets and bound the solution of models of reaction systems subject to uncertainties or disturbances in their parameters and inputs [73, 74]. The different applications of the rate decoupling provided by variants and invariants have been recently reviewed [75]. Finally, it is also worth mentioning that the use of the concept of extent of reaction in the chemical education has been a topic of active discussion [76, 77, 78].

1.3 Research Objectives

The general objectives of this doctoral work are (i) to develop the concept of variants and invariants, in particular for other reaction systems, and (ii) to find new applications of this concept that can improve process operation of reaction systems, namely through improved analysis, estimation, control and optimization. In that sense, this doctoral work can be seen as the continuation of the work developed by previous doctoral students from the same research group, namely Amrhein [34], Bhatt [24], and Srinivasan [79]. These applications could take advantage of the use of the concept of variants and invariants in the following ways: (a) to decouple the various rate processes and certain signals related to them, (b) to process measured data and reconstruct or predict, in the absence of a kinetic model, certain quantities that can then be used for identification and model-free estimation, control and optimization, and (c) to simplify the dynamic model, its analysis and the design of model-based estimation, control and optimization schemes. This doctoral work will investigate some areas that have been less developed so far, such as the transformation to variants and invariants in distributed reaction systems, the control of reaction systems in the presence and in the absence of kinetic models via the concept of variants and invariants, and the use of variants and invariants for optimization.

1.4 Organization and Main Contributions of the Thesis

The content and main contributions of the chapters that compose this thesis are summarized next.

Chapter 2: Concept of Variants and Invariants for Lumped Reaction Systems This chapter introduces the material and heat balances for several lumped reaction systems, the concept of variants and invariants, and the transformations used to obtain them. It starts with a discussion about the concepts of independent stoichiometries and reaction rates in Section 2.1, where it is shown that this independence can be assumed throughout the thesis without loss of generality. Then, in Section 2.2, the model of homogeneous lumped reaction systems is presented via the material balance and the heat balance, including for the particular case of batch and semi-batch homogeneous reactors. Similar models are developed

for other cases of lumped reaction systems, namely for reaction systems with instantaneous equilibria in Section 2.3 and multiphase reaction systems in Section 2.4. For the case of homogeneous lumped reaction systems, and without considering the heat balance, several transformations between quantities related to numbers of moles (including numbers of moles in variant and vessel-variant forms) and different definitions of variants and invariants are presented in Section 2.5, namely reaction variants and invariants, reaction and inlet variants and invariants, batch extents, and vessel extents. The transformation from measured quantities related to numbers of moles to extents and to reconciled quantities also related to number of moles is discussed. At the end of this chapter, several extensions of the concept of extents and of the transformation to extents are shown in Section 2.6, for homogeneous reaction systems described by concentrations, multiphase reaction systems, and several lumped reaction systems with combined material and heat balances.

Chapter 3: Concept of Extents for Distributed Reaction Systems This chapter generalizes the concept of extents discussed in the previous chapter to distributed reaction systems with and without energy balance, which are described by partial differential equations that depend on time and on one or more spatial coordinates. For each reaction system, the balance equations are written, the concept of extents is defined, and the transformation to extents is presented. Firstly, it is shown in Section 3.2 how to make the transition between a homogeneous lumped reactor and a single-phase plug-flow reactor, which is the simplest case of a distributed reaction system. Next, the discussion about the concept of extents continues with other cases of distributed reaction systems, such as single-phase and multiphase one-dimensional tubular reactors and multiphase two-dimensional tubular reactors in Section 3.3, as well as packed and tray reactive separation columns in Section 3.4. The concept of extents is generalized in Section 3.5 to generic distributed reaction systems, showing that the concept of extents and the transformation to extents exist in a generic framework that is independent of the configuration and operating conditions. At the end, in Section 3.6, several simulated case studies are presented for the cases of a single-phase plug-flow reactor, a single-phase one-dimensional tubular reactor, a packed reactive absorption column and a tray reactive distillation column.

Main contributions:

- The concept of extents and the transformation to extents are generalized to distributed reaction systems, such as tubular reactors, reactive separation columns, and generic distributed reaction systems.

Chapter 4: Estimation of Kinetic Parameters via the Incremental Approach This chapter presents a new development of the extent-based incremental approach for estimation of kinetic parameters, which can be used to guarantee global and maximum-likelihood parameter estimation. It starts by presenting in Section 4.2 the typical formulation of the

extent-based incremental approach, which allows one to identify each reaction individually, and reduce the number of parameters to identify via optimization to the ones that appear nonlinearly in the investigated rate law. For this, the extents are expressed as convolution integrals, and the structure of the rate law is described by separating the parameters that appear linearly and nonlinearly. Then, the identification problem is formulated as the comparison between experimental and modeled extents, it is shown that this problem can be reformulated only with the parameters that appear nonlinearly in the rate law as decision variables, and the method used to compute the solution is presented. Since this formulation of the incremental approach does not generate maximum-likelihood parameter estimates, two methods are proposed in Section 4.3 to address this issue: (i) a method to obtain uncorrelated experimental extents from uncorrelated measurements; and (ii) a method to obtain unbiased estimates of rates computed from experimental measurements, which results in unbiased modeled extents. It is proven that the use of these two methods results in maximum-likelihood parameter estimation when the sampling frequency is large enough. In addition, it is shown in Section 4.4 how to obtain global estimation of kinetic parameters with the extent-based incremental approach. For this, the rate law is approximated by a Taylor series expansion, and the approximate identification problem is reformulated as a polynomial optimization problem and as a convex problem, namely a semidefinite program. Then, it is proven that one can guarantee global and maximum-likelihood parameter estimation by computing the solution to this convex problem. Simulated examples illustrate the use of the methods in this chapter to obtain maximum-likelihood parameter estimation and to deal with identification problems with multiple local minima, namely in Section 4.5.

Main contributions:

- Methods to obtain uncorrelated experimental extents and unbiased estimates of rates computed from measurements are presented.
- The identification problem of the extent-based incremental approach is reformulated as a convex problem, using only the parameters that appear nonlinearly in the rate law as decision variables.
- The extent-based incremental approach can be used to guarantee global and maximum-likelihood estimation of kinetic parameters.

Chapter 5: Estimation of Rate Signals without Kinetic Models This chapter discusses the estimation of rate signals based on measurements and without the knowledge or the identification of their kinetic models, which exploits the fact that the concept of variants allows isolating the different rates. The general formulation of the dynamic system considered for rate estimation is introduced in Section 5.2, and it is shown how the rates can be isolated via transformation to variants and which assumptions are needed to compute these variants from available measurements. Since the rate estimation method presented in this chapter relies on numerical differentiation, a specific differentiation method, the

Savitzky-Golay filter, is described in Section 5.3, and analytical expressions are obtained for the error, variance and covariance of the differentiated signals. Then, it is shown in Section 5.4 that the rate estimator obtained with the differentiating Savitzky-Golay filter is the optimal rate estimator based on convolution filters. The transformation to variants that provides maximum-likelihood estimation of unknown rates is provided, and the resulting analytical expressions for the error and variance of the rate estimates are given.

Main contributions:

- The transformation to variants is used to isolate the rate signals and estimate them without identification of kinetic models.
- The optimal rate estimator based on convolution filters is obtained via numerical differentiation using a Savitzky-Golay filter.
- Analytical expressions for the error and variance of the rate estimates are given.

Chapter 6: Reactor Control This chapter shows how the concept of variants can be used for reactor control, both with and without kinetic models. In the case of control with kinetic models, two cases are presented in Section 6.2, both via feedback linearization, which provide either offset-free control of vessel extents using the model in terms of vessel extents or offset-free control of numbers of moles using the model in terms of numbers of moles. In the case of control without kinetic models, one takes advantage of rate estimation without kinetic models to implement a control scheme via feedback linearization in Section 6.3. After the description of the general dynamic system that is considered for control without kinetic models, the evolution of the controlled variables and inputs via feedback linearization is shown. As a consequence of the proposed design of the outer-loop feedback controller, it is shown that the expected values of controlled variables converge exponentially to their setpoints, and an expression for the variance of the controlled variables is also obtained. This allows assessing the stability of the closed-loop system, based on the expected value and variance of the controlled variables. Then, a simulated example of control of temperature and reactant concentrations in a CSTR illustrates the control scheme without kinetic models and compares it with other controllers.

Main contributions:

- Offset-free control of vessel extents and numbers of moles via feedback linearization is obtained using kinetic models.
- A reactor control scheme that does not rely on kinetic models is designed via rate estimation and feedback linearization.
- Convergence of the controlled variables to their setpoints and closed-loop stability is achieved without the use of kinetic models.

Chapter 7: Fast Steady-state Optimization of Dynamic Systems This chapter addresses the fast estimation of plant steady state for imperfectly known dynamic systems and its application to fast steady-state optimization. It starts by presenting in Section 7.2 the assumptions that need to be satisfied by the dynamic model considered for this approach, which result in the existence of fast and slow states and an unknown part of the dynamics that depends only on the fast states. For this type of dynamic systems, it is shown in Section 7.3 how measurement-based estimation of unknown rates without kinetic models can be obtained. Then, it is described in Section 7.4 how the use of feedback control and estimation of the unknown rates without kinetic models can be used to estimate the plant steady state during the transient of the slow part, as soon as feedback control enforces convergence of the fast part to steady state. The speed-up provided by feedback control of the fast states is quantified, and the use of control via feedback linearization and rate estimation for this purpose is described. The method used for steady-state estimation based on estimates of the unknown rates is presented, and the quality of these steady-state estimates is also quantified. The assumptions needed for the dynamic model with fast and slow states, the feedback control scheme, and the steady-state estimation method are shown to be realistic for the case of a generic continuous stirred-tank reactor (CSTR), where steady-state estimation can also be implemented directly via the concept of extents. The fast estimation of plant steady state is illustrated with a simulated example of a CSTR. In addition, the use of fast estimation of plant steady state for real-time steady-state optimization is described in Section 7.5. Several configurations for estimation of plant steady state are compared in the context of real-time optimization, showing that the configuration with feedback control and rate estimation is the fastest scheme. At the end, real-time steady-state optimization with fast steady-state estimation is also illustrated with an example of a CSTR, which shows that the optimization problem can be reformulated in terms of the fast part via rate estimation and how this measurement-based optimization method deals with the presence of measurement noise.

Main contributions:

- Fast estimation of plant steady state for imperfectly known dynamic systems with fast and slow states is implemented via the use of feedback control and rate estimation without kinetic models.
- The assumptions needed for fast estimation of plant steady state are shown to be realistic for continuous stirred-tank reactors.
- Fast steady-state optimization is achieved by combining real-time steady-state optimization with fast estimation of plant steady state via feedback control and rate estimation.

Chapter 8: Dynamic Optimization via Parsimonious Input Parameterization This chapter discusses the use of a parsimonious input parameterization for dynamic optimization, which takes advantage of the concept of extents in the cases of batch, semi-batch and contin-

uous reactors. The first step is the formulation of the relevant class of dynamic optimization problems in Section 8.2. Next, in Section 8.3, the analytical computation of adjoint-free optimal control laws is presented for all the types of arcs that may occur in the optimal solution, resulting in a finite set of plausible arc sequences. It is shown that this analytical computation may benefit from the use of the concept of extents to convert the model of batch, semi-batch and continuous reactors to a general framework. An alternative method to approximate the adjoint-free optimal control laws using cubic splines is also presented. Then, the generic idea of the approach used for parsimonious input parameterization of the optimal inputs is presented in Section 8.4, which allows describing the dynamic model for an arc sequence using switching times and initial conditions of certain arcs as input parameters. Details are given about the implementation of the numerical optimization method for an arc sequence that is used to find the optimal parameter values, and it is shown how one can use the solution to this optimization problem to verify whether the necessary conditions of optimality given by the Pontryagin's maximum principle are satisfied. The implications of the reduction in the number of decision variables for global dynamic optimization are discussed. Finally, some simulated examples are presented in Section 8.5 to illustrate the developed methods: maximization of the profit and minimization of the batch time of a chlorination reaction; maximization of the amount of product of an acetoacetylation reaction; maximization of the amount of distillate of a batch distillation column; and maximization of the amount of product of a non-isothermal reaction.

Main contributions:

- For a generic class of dynamic optimization problems, finite sets of plausible arc sequences are constructed, where each arc that may occur is described by an adjoint-free optimal control law.
- The analytical computation of adjoint-free optimal control laws is made possible using the concept of extents or approximations of these control laws via cubic splines.
- A parsimonious input parameterization that allows describing the dynamic model for an arc sequence with few parameters, namely switching times and initial conditions of the arcs, is presented.

Chapter 9: Conclusion. The main conclusions and contributions of the thesis are summarized, some final remarks are mentioned, and an outlook for future work is provided.

2 Concept of Variants and Invariants for Lumped Reaction Systems

Part of this chapter is adapted from the postprint of the following article [1]:

D. Rodrigues, S. Srinivasan, J. Billeter, and D. Bonvin. Variant and invariant states for chemical reaction systems. *Comput. Chem. Eng.*, 73:23–33, 2015.

Link: http://doi.org/10.1016/j.compchemeng.2014.10.009.

The author of this thesis contributed to that article by developing the main novel ideas and writing a significant part of the text. Hence, the author retains the right to include the article in this thesis since it is not published commercially and the journal is referenced as the original source.

2.1 Independent Reactions and Inlets

2.1.1 Reaction network

Let us consider a reaction system with S species living in the set $\mathscr{S} = \{\mathscr{X}_1, \ldots, \mathscr{X}_S\}$ and R_d reactions. The system can be represented by the following reaction network:

$$\sum_{s=1}^{S} \nu_{i,s}^{-} \mathscr{X}_s \rightarrow \sum_{s=1}^{S} \nu_{i,s}^{+} \mathscr{X}_s, \quad \forall i = 1, \ldots, R_d, \tag{2.1}$$

where $\nu_{i,s}^{-}$ and $\nu_{i,s}^{+}$ are nonnegative numbers that represent the relative consumption and production of the sth species by the ith reaction, for all $i = 1, \ldots, R_d$ and $s = 1, \ldots, S$. If $\nu_{i,s}^{-} > 0$, then the sth species is a reactant of the ith reaction; if $\nu_{i,s}^{+} > 0$, then the sth species is a product of the ith reaction.

The reaction network given above is quite general in the sense that it can be applied to any reaction system with constant stoichiometries. In the case of a reversible reaction, the reaction can be written as two irreversible reactions, one for the forward reaction and another for the backward reaction. In the case of a reaction with catalysts or autocatalysts,

these species can be included as a reactant and as a product in the same reaction.

The quantitative relationships among species that participate in reactions are known as stoichiometries. Hence, the net production of the sth species by the ith reaction is given by the stoichiometric coefficient $\nu_{i,s}$, defined as

$$\nu_{i,s} := \nu_{i,s}^{+} - \nu_{i,s}^{-}. \tag{2.2}$$

The stoichiometric matrix $\mathbf{N}_d$ of dimension $R_d \times S$ contains the stoichiometric coefficients and is defined as

$$\mathbf{N}_d := \begin{bmatrix} \nu_{1,1} & \cdots & \nu_{1,S} \\ \vdots & \vdots & \vdots \\ \nu_{R_d,1} & \cdots & \nu_{R_d,S} \end{bmatrix}. \tag{2.3}$$

The species in the reaction system are composed of a number of quantities that are conserved by the reactions, namely atoms of different elements and electrical charges. Let E_d denote the number of such conserved quantities living in the set $\mathscr{E}$, and let $\alpha_{s,e}$ denote the number of the eth conserved quantity in the sth species. The atomic matrix $\mathbf{A}$ of dimension $S \times E_d$ and rank $E > 0$ is then defined as

$$\mathbf{A} := \begin{bmatrix} \alpha_{1,1} & \cdots & \alpha_{1,E_d} \\ \vdots & \vdots & \vdots \\ \alpha_{S,1} & \cdots & \alpha_{S,E_d} \end{bmatrix}. \tag{2.4}$$

For any stoichiometric matrix $\mathbf{N}_d$, the R_d stoichiometries must satisfy a conservation equation for each one of the E_d conserved quantities, that is,

$$\mathbf{A}^{\mathrm{T}}\mathbf{N}_d^{\mathrm{T}} = \mathbf{0}_{E_d \times R_d}, \tag{2.5}$$

which implies that the columns of $\mathbf{N}_d^{\mathrm{T}}$ lie in the null space of $\mathbf{A}^{\mathrm{T}}$. Hence, the rank of $\mathbf{N}_d$, denoted as R_N, cannot be greater than the dimension of the null space of $\mathbf{A}^{\mathrm{T}}$.

Since $\mathbf{A}^{\mathrm{T}}$ has S columns, one can infer from the rank-nullity theorem that the dimension of the null space of $\mathbf{A}^{\mathrm{T}}$ is $S - E$, which implies that

$$R_N := \mathrm{rank}(\mathbf{N}_d) \leq S - E < S. \tag{2.6}$$

Now let $\mathbf{r}_d(t)$ denote the R_d-dimensional vector of reaction rates that correspond to the stoichiometric matrix $\mathbf{N}_d$. These reaction rates are typically functions of the S-dimensional vector $\mathbf{c}(t)$ of concentrations of the S species and of the temperature $T(t)$, which represent the so-called reaction kinetics, but they are modeled here as time-varying signals $\mathbf{r}_d(t)$, without the explicit dependence on $\mathbf{c}(t)$ and $T(t)$. One can observe that the net production of the S species by the reactions at time t is given by $\mathbf{N}_d^{\mathrm{T}} V(t) \mathbf{r}_d(t)$, where $V(t)$ is the volume.

2.1.2 Independent reactions

Note that the stoichiometries that correspond to the rows of the matrix $\mathbf{N}_d$ may be linearly independent or not. Furthermore, the reaction rates $\mathbf{r}_d(t)$ may be linearly independent or not over a given finite time interval $t \in [t_0, t_H]$. Ideally, one would like to describe the net production by the reactions with linearly independent stoichiometries and linearly independent reaction rates (over a time interval). In that case, we would obtain independent reactions, as described by the following definition [34]:

Definition 2.1 (Independent reactions)**.** Let the net production of the S species by R reactions at time t be given by $\mathbf{N}^{\mathrm{T}} V(t)\mathbf{r}(t)$, where $\mathbf{N}$ is an $R \times S$ stoichiometric matrix, $V(t)$ is the volume, and $\mathbf{r}(t)$ is an R-dimensional vector of reaction rates. The R reactions are said to be independent if (i) the rows of $\mathbf{N}$, that is, the stoichiometries, are linearly independent, and (ii) the reaction rates $\mathbf{r}(t)$ are linearly independent over a finite time interval $t \in [t_0, t_H]$, which is expressed by the condition $\boldsymbol{\beta}^{\mathrm{T}}\mathbf{r}(t) = 0, \forall t \in [t_0, t_H] \Leftrightarrow \boldsymbol{\beta} = \mathbf{0}_R$.

Hence, to obtain a model of the reaction system expressed only in terms of independent reactions, one needs to obtain independent stoichiometries and independent reaction rates.

2.1.3 Transformation to independent stoichiometries and reaction rates

Let us recall that $\mathbf{N}_d$ is an $R_d \times S$ stoichiometric matrix of rank R_N, where R_d is the number of (possibly linearly dependent) stoichiometries. The stoichiometries in the matrix $\mathbf{N}_d$ result from a linear combination, specified by an $R_d \times R_N$ matrix $\mathbf{L}_N$ of rank R_N, of R_N linearly independent stoichiometries, specified by an $R_N \times S$ matrix $\mathbf{N}$ of rank R_N, which can be written as

$$\mathbf{N}_d = \mathbf{L}_N \mathbf{N}. \tag{2.7}$$

Let also $\mathbf{R}_d$ denote the $R_d \times H$ matrix of reaction rates at the instants $t_1, \ldots, t_H$ of rank R_r, where R_d is the number of (possibly linearly dependent for $t \in \{t_1, \ldots, t_H\}$) reaction rates and $H > R_r$. The reaction rates in the matrix $\mathbf{R}_d$ result from a linear combination, specified by an $R_d \times R_r$ matrix $\mathbf{L}_r$ of rank R_r, of R_r linearly independent reaction rates, specified by an $R_r \times H$ matrix $\mathbf{R}$ of rank R_r, which can be written as

$$\mathbf{R}_d = \mathbf{L}_r \mathbf{R}. \tag{2.8}$$

Two methods are presented in Appendix A.1 to decompose any matrix $\mathbf{M}_d$ with R_d rows and rank R_s as

$$\mathbf{M}_d = \hat{\mathbf{L}}_s \hat{\mathbf{M}}, \tag{2.9}$$

where $\hat{\mathbf{L}}_s$ is an $R_d \times R_s$ matrix of rank R_s and $\hat{\mathbf{M}}$ is an $R_s \times C$ matrix of rank R_s, that is, with R_s linearly independent rows. Although a singular value decomposition could be used

for this purpose, the goal here is to look for a more physically meaningful decomposition in the context of independent reactions. Hence, these two methods can be used to obtain independent stoichiometries (upon replacing C by S, $\mathbf{M}$ by $\mathbf{N}$ and the subscript s by N) or independent reaction rates (upon replacing C by H, $\mathbf{M}$ by $\mathbf{R}$ and the subscript s by r).

Consequently, to obtain a model of the reaction system expressed only in terms of independent reactions, the following steps are taken:

1. (i) One finds a matrix $\hat{\mathbf{L}}_N$ with columns that are a basis of the null space of $\mathbf{K}_N^{\mathrm{T}}$, where $\mathbf{K}_N$ is a matrix with columns that are a basis of the null space of $\mathbf{N}_d^{\mathrm{T}}$, and one computes $\hat{\mathbf{N}} = \left(\hat{\mathbf{L}}_N^{\mathrm{T}}\hat{\mathbf{L}}_N\right)^{-1}\hat{\mathbf{L}}_N^{\mathrm{T}}\mathbf{N}_d$, or (ii) one verifies that there exists an $R_N \times S$ matrix $\hat{\mathbf{N}}$ of independent stoichiometries and of rank R_N such that $\mathbf{N}_d = \mathbf{N}_d\hat{\mathbf{N}}^{\mathrm{T}}\left(\hat{\mathbf{N}}\hat{\mathbf{N}}^{\mathrm{T}}\right)^{-1}\hat{\mathbf{N}}$, and one computes $\hat{\mathbf{L}}_N = \mathbf{N}_d\hat{\mathbf{N}}^{\mathrm{T}}\left(\hat{\mathbf{N}}\hat{\mathbf{N}}^{\mathrm{T}}\right)^{-1}$. In both cases (i) and (ii), $\hat{\mathbf{L}}_N$ is an $R_d \times R_N$ matrix of rank R_N, $\hat{\mathbf{N}}$ is an $R_N \times S$ matrix of rank R_N, and

$$\mathbf{N}_d = \hat{\mathbf{L}}_N\hat{\mathbf{N}}. \tag{2.10}$$

2. (i) One finds a matrix $\hat{\mathbf{L}}_r$ with columns that are a basis of the null space of $\mathbf{K}_r^{\mathrm{T}}$, where $\mathbf{K}_r$ is a matrix with columns that are a basis of the null space of $\mathbf{R}_d^{\mathrm{T}}$, and one computes $\hat{\mathbf{R}} = \left(\hat{\mathbf{L}}_r^{\mathrm{T}}\hat{\mathbf{L}}_r\right)^{-1}\hat{\mathbf{L}}_r^{\mathrm{T}}\mathbf{R}_d$, or (ii) one verifies that there exists an $R_r \times H$ matrix $\hat{\mathbf{R}}$ of independent reaction rates and of rank R_r such that $\mathbf{R}_d = \mathbf{R}_d\hat{\mathbf{R}}^{\mathrm{T}}\left(\hat{\mathbf{R}}\hat{\mathbf{R}}^{\mathrm{T}}\right)^{-1}\hat{\mathbf{R}}$, and one computes $\hat{\mathbf{L}}_r = \mathbf{R}_d\hat{\mathbf{R}}^{\mathrm{T}}\left(\hat{\mathbf{R}}\hat{\mathbf{R}}^{\mathrm{T}}\right)^{-1}$. In both cases (i) and (ii), $\hat{\mathbf{L}}_r$ is an $R_d \times R_r$ matrix of rank R_r, $\hat{\mathbf{R}}$ is an $R_r \times H$ matrix of rank R_r, and

$$\mathbf{R}_d = \hat{\mathbf{L}}_r\hat{\mathbf{R}}. \tag{2.11}$$

Note that this implies that there exists an R_r-dimensional vector of independent reaction rates $\hat{\mathbf{r}}(t)$ (for $t \in \{t_1, \ldots, t_H\}$) such that

$$\mathbf{r}_d(t_h) = \hat{\mathbf{L}}_r\hat{\mathbf{r}}(t_h), \quad \forall h = 1, \ldots, H. \tag{2.12}$$

3. At this point, one can write that

$$\mathbf{N}_d^{\mathrm{T}}\mathbf{r}_d(t_h) = \hat{\mathbf{N}}^{\mathrm{T}}\hat{\mathbf{L}}_N^{\mathrm{T}}\hat{\mathbf{L}}_r\hat{\mathbf{r}}(t_h), \quad \forall h = 1, \ldots, H. \tag{2.13}$$

Let us define the number of independent reactions $R = \min(R_N, R_r)$. Then, there are two cases:
(i) if $R_N = R$, then

$$\mathbf{N} = \hat{\mathbf{N}}, \tag{2.14}$$

$$\mathbf{r}(t) = \hat{\mathbf{L}}_N^{\mathrm{T}}\hat{\mathbf{L}}_r\hat{\mathbf{r}}(t), \tag{2.15}$$

or (ii) if $R_N > R$, then

$$\mathbf{N} = \hat{\mathbf{L}}_r^{\mathrm{T}} \hat{\mathbf{L}}_N \hat{\mathbf{N}}, \tag{2.16}$$

$$\mathbf{r}(t) = \hat{\mathbf{r}}(t). \tag{2.17}$$

In both cases (i) and (ii), $\mathbf{N}$ is an $R \times S$ matrix of rank R, $\mathbf{r}(t)$ is an R-dimensional vector such that $\boldsymbol{\beta}^{\mathrm{T}} \mathbf{r}(t) = 0, \forall t \in [t_0, t_H] \Leftrightarrow \boldsymbol{\beta} = \mathbf{0}_R$, and

$$\mathbf{N}_d^{\mathrm{T}} \mathbf{r}_d(t_h) = \mathbf{N}^{\mathrm{T}} \mathbf{r}(t_h), \quad \forall h = 1, \ldots, H. \tag{2.18}$$

Since it is known that the number of linearly independent stoichiometries is less than the number of species, that is, $R_N < S$, and $R \leq R_N$ by definition of R, the number of independent reactions is less than the number of species, that is, $R < S$.

In summary, one can assume without loss of generality that:

1. There are R independent reactions, and the number of independent reactions is less than the number of species, that is, $R < S$.
2. The stoichiometric matrix $\mathbf{N}$ is of dimension $R \times S$ and of rank R.
3. The vector of reaction rates $\mathbf{r}(t)$ is of dimension R, and these R reaction rates are independent over any given time interval.

2.1.4 Independent inlets

As mentioned above for the case of independent reactions, one would like to describe the net supply by the inlet flows with linearly independent inlet compositions and linearly independent inlet flowrates (over a time interval). In that case, we would obtain independent inlets, as described by the following definition:

Definition 2.2 (Independent inlets)**.** Let the net supply of the S species by p inlets at time t be given by $\mathbf{W}_{in}\mathbf{u}_{in}(t)$, where $\mathbf{W}_{in}$ is an $S \times p$ inlet-composition matrix and $\mathbf{u}_{in}(t)$ is a p-dimensional vector of inlet flowrates. The p inlets are said to be independent if (i) the columns of $\mathbf{W}_{in}$, that is, the inlet compositions, are linearly independent, and (ii) the inlet flowrates $\mathbf{u}_{in}(t)$ are linearly independent over a finite time interval $t \in [t_0, t_H]$, which is expressed by the condition $\boldsymbol{\beta}^{\mathrm{T}} \mathbf{u}_{in}(t) = 0, \forall t \in [t_0, t_H] \Leftrightarrow \boldsymbol{\beta} = \mathbf{0}_p$.

To obtain a model of the reaction system expressed only in terms of independent inlets, one needs to obtain independent inlet compositions and inlet flowrates, as shown for the case of independent reactions.

2.2 Model of Homogeneous Reaction Systems

Let us consider an open homogeneous reactor with S species, R independent reactions, p independent inlets and one outlet.

2.2.1 Material balance equations, $\mathbf{n}(t)$

The material balance is expressed by the S-dimensional vector $\mathbf{n}(t)$ of numbers of moles of the S species, which are given by the ordinary differential equations (ODEs)

$$\dot{\mathbf{n}}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}(t)\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}(t), \qquad \mathbf{n}(0) = \mathbf{n}_0, \tag{2.19}$$

where $\mathbf{r}_v(t) := V(t)\mathbf{r}(t)$, with $V(t)$ the volume and $\mathbf{r}(t)$ the R-dimensional vector of reaction rates, $\mathbf{u}_{in}(t)$ is the p-dimensional vector of inlet mass flowrates, $\omega(t) := \frac{u_{out}(t)}{m(t)}$ is the inverse of the residence time, with $u_{out}(t)$ the outlet mass flowrate and $m(t)$ the mass, $\mathbf{N}$ is the $R \times S$ stoichiometric matrix, $\mathbf{W}_{in}(t)$ is the $S \times p$ matrix of compositions of the inlets, whose jth column is $\mathbf{W}_{in,j}(t) := \mathbf{M}_w^{-1}\check{\mathbf{w}}_{in,j}(t)$, with $\mathbf{M}_w$ the S-dimensional diagonal matrix of molecular weights and $\check{\mathbf{w}}_{in,j}(t)$ the S-dimensional vector of weight fractions of the jth inlet, and $\mathbf{n}_0$ are the initial numbers of moles.

This material balance holds independently of the operating conditions, that is, the way the variables $\mathbf{u}_{in}(t)$ and $u_{out}(t)$ are manipulated according to a control objective, or the way the reaction rates $\mathbf{r}(t)$ vary due to the concentrations and temperature. Hence, this material balance is also valid for nonisothermal homogeneous reactors.

The mass balance could be computed by the continuity equation

$$\dot{m}(t) = \mathbf{1}_p^{\mathrm{T}}\mathbf{u}_{in}(t) - \omega(t)m(t), \qquad m(0) = m_0, \tag{2.20}$$

where m_0 is the initial mass. However, by expressing the mass as

$$m(t) = \mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{n}(t), \tag{2.21}$$

one can observe that this mass balance and the material balance in Eq. (2.19) are linearly dependent.

If necessary, the concentrations $\mathbf{c}(t)$ can be computed from the numbers of moles as $\mathbf{c}(t) = \frac{\mathbf{n}(t)}{V(t)}$, with the volume given by $V(t) = \frac{m(t)}{\rho(t)}$, where the density $\rho(t)$ is a function of the concentrations and temperature. Hence, the concentrations can also be described by the following ODEs:

$$\begin{aligned}
\dot{\mathbf{c}}(t) &= \frac{\dot{\mathbf{n}}(t)}{V(t)} - \frac{\dot{V}(t)}{V(t)}\mathbf{c}(t) \\
&= \frac{1}{V(t)}\left(\mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}(t)\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}(t)\right) - \frac{\dot{V}(t)}{V(t)}\mathbf{c}(t) \\
&= \mathbf{N}^{\mathrm{T}}\mathbf{r}(t) + \mathbf{W}_{in}(t)\frac{\mathbf{u}_{in}(t)}{V(t)} - \left(\omega(t) + \frac{\dot{V}(t)}{V(t)}\right)\mathbf{c}(t), \qquad \mathbf{c}(0) = \frac{\mathbf{n}_0}{V_0},
\end{aligned} \tag{2.22}$$

where

$$\omega(t) + \frac{\dot{V}(t)}{V(t)} = \omega(t) + \frac{\dot{m}(t)}{m(t)} - \frac{\dot{\rho}(t)}{\rho(t)} = \frac{\mathbf{1}_p^{\mathrm{T}}\mathbf{u}_{in}(t)}{m(t)} - \frac{\dot{\rho}(t)}{\rho(t)}. \tag{2.23}$$

Note that the concentrations $\mathbf{c}(t)$ are dependent since the concentration of one species is determined by the remaining $S-1$ concentrations, which means that only $S-1$ concentrations are needed as states and only $S-1$ of the ODEs (2.22) are necessary. This can be shown by noticing that the concentrations are subject to the constraint

$$\rho(t) = \frac{m(t)}{V(t)} = \frac{\mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{n}(t)}{V(t)} = \mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{c}(t), \tag{2.24}$$

with $\rho(t)$ a function of the concentrations and temperature. However, one additional state is needed to express the dimension of the system, for example $m(t)$, thus the number of states needed to fully describe the system is S.

2.2.2 Heat balance equation, $Q(t)$

The energy balance is expressed by the enthalpy $H(t)$, which is given by the ODE

$$\dot{H}(t) = q_{ex}(t) + \mathbf{h}_{in}(t)^{\mathrm{T}}\mathbf{u}_{in}(t) - \omega(t)H(t), \qquad H(0) = H_0, \tag{2.25}$$

where $q_{ex}(t)$ is the exchanged heat power, and $\mathbf{h}_{in}(t)$ is the p-dimensional vector of specific enthalpies of the inlets. The enthalpy $H(t)$ depends on the reactor temperature $T(t)$, the reactor pressure $P(t)$ and the numbers of moles $\mathbf{n}(t)$. The exchanged heat power $q_{ex}(t)$ includes different sources, namely:

- The power exchanged with a heating/cooling jacket, given by the term $UA(T_j(t) - T(t))$, where U is the overall heat transfer coefficient, A is the heat transfer area, and $T_j(t)$ is the jacket temperature.
- The power dissipated by the stirrer, given by the term $M(t)\dot{\phi}(t)$, where $M(t)$ is the stirrer torque and $\dot{\phi}(t)$ is its angular speed.
- The compression work, given by the term $V(t)\dot{P}(t)$.

Let us assume that the enthalpies of mixing are negligible, and let $\mathbf{H}_m(T,P)$ denote the S-dimensional vector of molar enthalpies of the S species at the temperature T and pressure p. Then, the enthalpy is given by

$$H(t) = \mathbf{H}_m(T(t),P(t))^{\mathrm{T}}\mathbf{n}(t), \tag{2.26}$$

and the specific enthalpies of the inlets are given by

$$h_{in,j}(t) = \mathbf{H}_m(T_{in,j}(t),P_{in,j}(t))^{\mathrm{T}}\mathbf{W}_{in,j}(t), \quad \forall j = 1,\ldots,p, \tag{2.27}$$

where $T_{in,j}(t)$ and $P_{in,j}(t)$ are the temperature and the pressure of the jth inlet.

The molar enthalpies are such that

$$\frac{\partial \mathbf{H}_m}{\partial T}(T,P) = \mathbf{c}_p(T,P), \tag{2.28}$$

$$\frac{\partial \mathbf{H}_m}{\partial P}(T,P) = \mathbf{v}_m(T,P) - \frac{\partial \mathbf{v}_m}{\partial T}(T,p)T, \tag{2.29}$$

with $\mathbf{c}_p(T,P)$ and $\mathbf{v}_m(T,P)$ the S-dimensional vectors of molar heat capacities at constant pressure and molar volumes, at the temperature T and pressure P, for the state of matter of the homogeneous phase.

Let us assume that the molar enthalpies do not depend on the pressure, that is,

$$\frac{\partial \mathbf{H}_m}{\partial P}(T,P) = \mathbf{0}_S, \tag{2.30}$$

which implies that the molar heat capacities at constant pressure do not depend on the pressure either since

$$\frac{\partial \mathbf{c}_p}{\partial P}(T,P) = \frac{\partial}{\partial P}\left(\frac{\partial \mathbf{H}_m}{\partial T}(T,P)\right) = \frac{\partial}{\partial T}\left(\frac{\partial \mathbf{H}_m}{\partial P}(T,P)\right) = \mathbf{0}_S. \tag{2.31}$$

The enthalpy can also be expressed in differential form as

$$\dot{H}(t) = \frac{\partial \mathbf{H}_m}{\partial T}(T(t),P(t))^{\mathrm{T}}\mathbf{n}(t)\dot{T}(t) + \mathbf{H}_m(T(t),P(t))^{\mathrm{T}}\dot{\mathbf{n}}(t), \tag{2.32}$$

which implies that the energy balance can be written as

$$\mathbf{c}_p(T(t),P_{ref})^{\mathrm{T}}\mathbf{n}(t)\dot{T}(t) + \mathbf{H}_m(T(t),P_{ref})^{\mathrm{T}}\dot{\mathbf{n}}(t) = q_{ex}(t) + \mathbf{h}_{in}(t)^{\mathrm{T}}\mathbf{u}_{in}(t) - \omega(t)H(t), \tag{2.33}$$

where P_{ref} is the reference pressure.

Let us now define the difference of the specific enthalpies of the inlets with respect to the reactor as

$$\begin{aligned}\Delta^T h_{in,j}(t) &:= \left(\mathbf{H}_m(T_{in,j}(t),P_{ref}) - \mathbf{H}_m(T(t),P_{ref})\right)^{\mathrm{T}}\mathbf{W}_{in,j}(t) \\ &= \int_{T(t)}^{T_{in,j}(t)} \mathbf{c}_p(\theta,P_{ref})^{\mathrm{T}}\mathbf{W}_{in,j}(t)\,\mathrm{d}\theta, \quad \forall j = 1,\ldots,p,\end{aligned} \tag{2.34}$$

which implies that

$$\Delta^T \mathbf{h}_{in}(t)^{\mathrm{T}} = \mathbf{h}_{in}(t)^{\mathrm{T}} - \mathbf{H}_m(T(t),P_{ref})^{\mathrm{T}}\mathbf{W}_{in}(t), \tag{2.35}$$

and let $\Delta\mathbf{H}$ denote the S-dimensional vector of molar enthalpies of formation of the S species at the reference temperature T_{ref} and pressure P_{ref}.

Then, the energy balance is expressed by the temperature $T(t)$, which is given by the ODE

$$\begin{aligned}\dot{T}(t) &= \frac{q_{ex}(t) + \mathbf{h}_{in}(t)^{\mathrm{T}}\mathbf{u}_{in}(t) - \omega(t)H(t)}{\mathbf{c}_p(T(t), P_{ref})^{\mathrm{T}}\mathbf{n}(t)} \\ &\quad - \mathbf{H}_m(T(t), P_{ref})^{\mathrm{T}}\frac{\mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}(t)\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}(t)}{\mathbf{c}_p(T(t), P_{ref})^{\mathrm{T}}\mathbf{n}(t)} \\ &= \frac{-\Delta^T\mathbf{H}_r(t)^{\mathrm{T}}\mathbf{r}_v(t) + q_{ex}(t) + \Delta^T\mathbf{h}_{in}(t)^{\mathrm{T}}\mathbf{u}_{in}(t)}{\mathbf{c}_p(T(t), P_{ref})^{\mathrm{T}}\mathbf{n}(t)}, \qquad T(0) = T_0, \end{aligned} \tag{2.36}$$

where

$$\begin{aligned}\Delta^T\mathbf{H}_r(t) &:= \mathbf{N}\mathbf{H}_m(T(t), P_{ref}) \\ &= \mathbf{N}\mathbf{H}_{m,ref} + \mathbf{N}\big(\mathbf{H}_m(T(t), P_{ref}) - \mathbf{H}_m(T_{ref}, P_{ref})\big) \\ &= \mathbf{N}\left(\Delta\mathbf{H} + \int_{T_{ref}}^{T(t)} \mathbf{c}_p(\theta, P_{ref})\mathrm{d}\theta\right)\end{aligned} \tag{2.37}$$

is the R-dimensional vector of enthalpies of reaction at $T(t)$, with $\mathbf{H}_{m,ref} := \mathbf{H}_m(T_{ref}, P_{ref})$ the molar enthalpies of the species at the reference temperature T_{ref} and pressure P_{ref}. Note that $\Delta^T\mathbf{H}_r(t)$ is not constant, and $\Delta^T\mathbf{h}_{in}(t)$ is not constant either even if the composition and temperature of the inlets are constant, because they depend on the reactor temperature $T(t)$.

Note that it would also be possible to write the enthalpy as

$$H(t) = \mathbf{H}_{m,ref}^{\mathrm{T}}\mathbf{n}(t) + \bar{\mathbf{c}}_p(t)^{\mathrm{T}}\mathbf{n}(t)\left(T(t) - T_{ref}\right), \tag{2.38}$$

where $\bar{\mathbf{c}}_p(t) := \int_{T_{ref}}^{T(t)} \mathbf{c}_p(\theta, P_{ref})\mathrm{d}\theta / \left(T(t) - T_{ref}\right)$ is the S-dimensional vector of average molar heat capacities at constant pressure between $T(t)$ and T_{ref}, and the specific enthalpies of the inlets as

$$h_{in,j}(t) = \mathbf{H}_{m,ref}^{\mathrm{T}}\mathbf{W}_{in,j}(t) + \bar{\mathbf{c}}_{p,in,j}(t)^{\mathrm{T}}\mathbf{W}_{in,j}(t)\left(T_{in,j}(t) - T_{ref}\right), \quad \forall j = 1, \ldots, p, \tag{2.39}$$

where $\bar{\mathbf{c}}_{p,in,j}(t) := \int_{T_{ref}}^{T_{in,j}(t)} \mathbf{c}_p(\theta, P_{ref})\mathrm{d}\theta / \left(T_{in,j}(t) - T_{ref}\right)$ is the S-dimensional vector of average molar heat capacities at constant pressure between $T_{in,j}(t)$ and T_{ref}.

Let us define the heat as

$$Q(t) := \bar{\mathbf{c}}_p(t)^{\mathrm{T}}\mathbf{n}(t)\left(T(t) - T_{ref}\right), \tag{2.40}$$

and the specific heats of the inlets as

$$\check{T}_{in,j}(t) := \bar{\mathbf{c}}_{p,in,j}(t)^{\mathrm{T}}\mathbf{W}_{in,j}(t)\left(T_{in,j}(t) - T_{ref}\right), \quad \forall j = 1,\ldots,p, \tag{2.41}$$

which implies that

$$Q(t) = H(t) - \mathbf{H}_{m,ref}^{\mathrm{T}}\mathbf{n}(t), \tag{2.42}$$

and

$$\check{\mathbf{T}}_{in}(t)^{\mathrm{T}} = \mathbf{h}_{in}(t)^{\mathrm{T}} - \mathbf{H}_{m,ref}^{\mathrm{T}}\mathbf{W}_{in}(t). \tag{2.43}$$

Hence, the heat balance can also be expressed by the heat $Q(t)$, according to

$$\begin{aligned}
\dot{Q}(t) &= \dot{H}(t) - \mathbf{H}_{m,ref}^{\mathrm{T}}\dot{\mathbf{n}}(t) \\
&= q_{ex}(t) + \mathbf{h}_{in}(t)^{\mathrm{T}}\mathbf{u}_{in}(t) - \omega(t)H(t) \\
&\quad - \mathbf{H}_{m,ref}^{\mathrm{T}}\left(\mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}(t)\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}(t)\right) \\
&= -\Delta\mathbf{H}_r^{\mathrm{T}}\mathbf{r}_v(t) + q_{ex}(t) + \check{\mathbf{T}}_{in}(t)^{\mathrm{T}}\mathbf{u}_{in}(t) - \omega(t)Q(t), \\
&\qquad\qquad Q(0) = Q_0 := \bar{\mathbf{c}}_{p,0}^{\mathrm{T}}\mathbf{n}_0\left(T_0 - T_{ref}\right),
\end{aligned} \tag{2.44}$$

where $\Delta\mathbf{H}_r := \mathbf{N}\mathbf{H}_{m,ref} = \mathbf{N}\Delta\mathbf{H}$ is the R-dimensional vector of enthalpies of reaction at T_{ref}. Note that $\Delta\mathbf{H}_r$ is constant, and $\check{\mathbf{T}}_{in}(t)$ is also constant if the composition and temperature of the inlets are constant.

Note that one can combine the material and heat balances by describing the system with the states $\mathbf{z}(t) := \begin{bmatrix}\mathbf{n}(t)\\ Q(t)\end{bmatrix}$.

2.2.3 Balances in batch and semi-batch homogeneous reactors

In the case of batch homogeneous reactors, there are no inlets and no outlet, which implies that $p = 0$ and $\omega(t) = 0$. Hence, the material balance expressed by the numbers of moles is given by

$$\dot{\mathbf{n}}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t), \qquad \mathbf{n}(0) = \mathbf{n}_0, \tag{2.45}$$

whereas the heat balance expressed by the heat is given by

$$\dot{Q}(t) = -\Delta\mathbf{H}_r^{\mathrm{T}}\mathbf{r}_v(t) + q_{ex}(t), \qquad Q(0) = Q_0. \tag{2.46}$$

In the case of semi-batch homogeneous reactors, there is at least one inlet and no outlet, which implies that $p > 0$ and $\omega(t) = 0$.[1] Hence, the material balance expressed by the

[1] Although the reactors with an outlet and no inlets are also classified in the literature as semi-batch reactors,

numbers of moles is given by

$$\dot{\mathbf{n}}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}(t)\mathbf{u}_{in}(t), \qquad \mathbf{n}(0) = \mathbf{n}_0, \tag{2.47}$$

whereas the heat balance expressed by the heat is given by

$$\dot{Q}(t) = -\Delta\mathbf{H}_r^{\mathrm{T}}\mathbf{r}_v(t) + q_{ex}(t) + \check{\mathbf{T}}_{in}(t)^{\mathrm{T}}\mathbf{u}_{in}(t), \qquad Q(0) = Q_0. \tag{2.48}$$

2.3 Model of Reaction Systems with Instantaneous Equilibria

Let us assume that, in an open homogeneous reactor, R_e reaction rates $\mathbf{r}_e(t)$ are fast (with instantaneous equilibrium) and R_s reaction rates $\mathbf{r}_s(t)$ are slow. Furthermore, the fast reaction rates are given by

$$\mathbf{r}_e(t) = \frac{1}{\epsilon}\boldsymbol{\varphi}_e\big(\mathbf{n}(t), Q(t)\big), \tag{2.49}$$

where ϵ is a small parameter and $\boldsymbol{\varphi}_e\big(\mathbf{n}(t), Q(t)\big)$ is an R_e-dimensional vector.

2.3.1 Material balance equations, $\mathbf{n}_s(t)$

Let us consider the material balance discussed in Section 2.2. The classification of the reaction rates as fast and slow allows us to write the dynamic model in Eq. (2.19) as

$$\dot{\mathbf{n}}(t) = \mathbf{N}_e^{\mathrm{T}}\frac{V(t)}{\epsilon}\boldsymbol{\varphi}_e\big(\mathbf{n}(t), Q(t)\big) + \boldsymbol{\phi}_s(t) - \omega(t)\mathbf{n}(t), \qquad \mathbf{n}(0) = \mathbf{n}_0, \tag{2.50}$$

where

$$\boldsymbol{\phi}_s(t) := \mathbf{N}_s^{\mathrm{T}}\mathbf{r}_{v,s}(t) + \mathbf{W}_{in}(t)\mathbf{u}_{in}(t), \tag{2.51}$$

with $\mathbf{r}_{v,s}(t) := V(t)\mathbf{r}_s(t)$.

Upon defining the fast time scale $\tau = \frac{t}{\epsilon}$, this system takes the form

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\mathbf{n}(t) = \mathbf{N}_e^{\mathrm{T}}V(t)\boldsymbol{\varphi}_e\big(\mathbf{n}(t), Q(t)\big) + \epsilon\Big(\boldsymbol{\phi}_s(t) - \omega(t)\mathbf{n}(t)\Big), \tag{2.52}$$

which implies that, when $\epsilon \to 0$, the fast dynamics of the system are described by

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\mathbf{n}(t) = \mathbf{N}_e^{\mathrm{T}}V(t)\boldsymbol{\varphi}_e\big(\mathbf{n}(t), Q(t)\big). \tag{2.53}$$

Let us assume that the rank of the matrix $\mathbf{N}_e^{\mathrm{T}}$ is R_e, that is, it has full column rank, which can always be achieved via appropriate choice of the stoichiometries and reaction

in the remainder of this thesis the concept of semi-batch reactors refers only to the reactors with at least one inlet and no outlet, also known as fed-batch reactors.

rates according to the results in Section 2.1. Then, the quasi-steady-state constraints for the system take the form

$$\mathbf{0}_{R_e} = \boldsymbol{\varphi}_e\big(\mathbf{n}(t), Q(t)\big). \tag{2.54}$$

The system of differential-algebraic equations (DAEs) given by the differential equation (2.50) and algebraic equation (2.54), which describes the slow dynamics of the system, is of high index and leads to an indetermination that is typically handled via differentiation of Eq. (2.54). The following alternative method is designed to deal with this situation.

The null space of the matrix $\mathbf{N}_e$ of rank R_e has the dimension $q_e := S - R_e$. Let the $S \times q_e$ matrix $\mathbf{P}_e$ be such that its columns span the null space of $\mathbf{N}_e$, that is, $\mathbf{N}_e\mathbf{P}_e = \mathbf{0}_{R_e \times q_e}$. Then, one can define the $S_s = q_e$ *numbers of moles of slow components* that are unaffected by the fast reactions as

$$\mathbf{n}_s(t) = \mathbf{P}_e^{\mathrm{T}}\mathbf{n}(t), \tag{2.55}$$

and write the corresponding slow dynamics as

$$\dot{\mathbf{n}}_s(t) = \mathbf{P}_e^{\mathrm{T}}\left(\mathbf{N}_s^{\mathrm{T}}\mathbf{r}_{v,s}(t) + \mathbf{W}_{in}(t)\mathbf{u}_{in}(t)\right) - \omega(t)\mathbf{n}_s(t), \qquad \mathbf{n}_s(0) = \mathbf{P}_e^{\mathrm{T}}\mathbf{n}_0, \tag{2.56}$$

which are independent of the fast reactions.

2.3.2 Heat balance equation, $Q_s(t)$

Let us consider the heat balance discussed in Section 2.2. The classification of the reaction rates as fast and slow allows us to write the dynamic model in Eq. (2.44) as

$$\dot{Q}(t) = -\Delta\mathbf{H}_{r,e}^{\mathrm{T}}\frac{V(t)}{\epsilon}\boldsymbol{\varphi}_e\big(\mathbf{n}(t), Q(t)\big) + \psi_s(t) - \omega(t)Q(t), \qquad Q(0) = Q_0, \tag{2.57}$$

where

$$\psi_s(t) := -\Delta\mathbf{H}_{r,s}^{\mathrm{T}}\mathbf{r}_{v,s}(t) + q_{ex}(t) + \check{\mathbf{T}}_{in}(t)^{\mathrm{T}}\mathbf{u}_{in}(t), \tag{2.58}$$

with $\mathbf{r}_{v,s}(t) := V(t)\mathbf{r}_s(t)$.

Upon defining the fast time scale $\tau = \frac{t}{\epsilon}$, this system takes the form

$$\frac{\mathrm{d}}{\mathrm{d}\tau}Q(t) = -\Delta\mathbf{H}_{r,e}^{\mathrm{T}}V(t)\boldsymbol{\varphi}_e\big(\mathbf{n}(t), Q(t)\big) + \epsilon\Big(\psi_s(t) - \omega(t)Q(t)\Big), \tag{2.59}$$

which implies that, when $\epsilon \to 0$, the fast dynamics of the system are described by

$$\frac{\mathrm{d}}{\mathrm{d}\tau}Q(t) = -\Delta\mathbf{H}_{r,e}^{\mathrm{T}}V(t)\boldsymbol{\varphi}_e\big(\mathbf{n}(t), Q(t)\big). \tag{2.60}$$

Let the S-dimensional vector $\Delta\mathbf{H}_e$ be such that $\mathbf{N}_e\Delta\mathbf{H}_e = \Delta\mathbf{H}_{r,e}$. Then, one can define the *slow heat* that is unaffected by the fast reactions as

$$Q_s(t) = \Delta\mathbf{H}_e^{\mathrm{T}}\mathbf{n}(t) + Q(t), \tag{2.61}$$

and write the corresponding slow dynamics as

$$\begin{aligned}\dot{Q}_s(t) = \Delta\mathbf{H}_e^{\mathrm{T}}\left(\mathbf{N}_s^{\mathrm{T}}\mathbf{r}_{v,s}(t) + \mathbf{W}_{in}(t)\mathbf{u}_{in}(t)\right) - \Delta\mathbf{H}_{r,s}^{\mathrm{T}}\mathbf{r}_{v,s}(t) + q_{ex}(t) + \check{\mathbf{T}}_{in}(t)^{\mathrm{T}}\mathbf{u}_{in}(t) \\ - \omega(t)Q_s(t), \qquad Q_s(0) = \Delta\mathbf{H}_e^{\mathrm{T}}\mathbf{n}_0 + Q_0,\end{aligned} \tag{2.62}$$

which is independent of the fast reactions.

Note that one can combine the material and heat balances by describing the system with the states $\mathbf{z}_s(t) := \begin{bmatrix}\mathbf{n}_s(t) \\ Q_s(t)\end{bmatrix}$.

2.3.3 Computation of solutions

It still needs to be shown how one could obtain the solution $\mathbf{n}(t)$ and $Q(t)$ for the right-hand side of Eqs. (2.56) and (2.62) from $\mathbf{z}_s(t)$. For this, one can use the R_e equations in Eq. (2.54), the S_s equations in Eq. (2.55), and the equation in Eq. (2.61) to obtain the $R_e + S_s + 1 = S + 1$ variables $\mathbf{n}(t)$ and $Q(t)$, provided that $\begin{bmatrix}\frac{\partial\boldsymbol{\varphi}_e}{\partial\mathbf{n}}(\mathbf{n}(t),Q(t)) & \frac{\partial\boldsymbol{\varphi}_e}{\partial Q}(\mathbf{n}(t),Q(t)) \\ \mathbf{P}_e^{\mathrm{T}} & \mathbf{0}_{S_s} \\ \Delta\mathbf{H}_e^{\mathrm{T}} & 1\end{bmatrix}$ is nonsingular along the solution.

Hence, the system of DAEs given by the differential equations (2.56) and (2.62) and algebraic equations (2.54), (2.55) and (2.61), which describes the slow dynamics of the system, is of index 1. This implies that its solution does not require time differentiation. Note that this is an extension of what had been shown previously only in the case of isothermal reaction systems [53]. Nevertheless, Appendix A.2 shows that the solution of the system of DAEs of index 1 is the same as the solution obtained via differentiation of Eq. (2.54).

2.4 Model of Multiphase Reaction Systems

Let us now consider an open reactor with multiple phases. Let us also assume that the reactor is lumped, that is, each phase is well mixed, the reactions take place only in the bulk of each phase, and each phase exchanges material with the other phases by mean of steady-state mass transfer, that is, with no accumulation in the boundary layers. The subscript $(\cdot)_f$ denotes quantities that are related to each phase F, where there are S_f species, R_f independent reactions, $p_{m,f}$ mass transfers (that is, species transferring to or from phase F), p_f independent inlets and one outlet.

2.4.1 Material balance equations, $\mathbf{n}_f(t)$

The material balance for phase F is expressed by the S_f-dimensional vector $\mathbf{n}_f(t)$ of numbers of moles of the S_f species in phase F, which are given by the ODEs

$$\begin{aligned}\dot{\mathbf{n}}_f(t) = \mathbf{N}_f^{\mathrm{T}}\mathbf{r}_{v,f}(t) + \mathbf{E}_{m,f}\boldsymbol{\phi}_{m,f}^{v}(t) + \mathbf{W}_{in,f}(t)\mathbf{u}_{in,f}(t) - \omega_f(t)\mathbf{n}_f(t),\\ \mathbf{n}_f(0) = \mathbf{n}_{f,0},\end{aligned} \tag{2.63}$$

where $\mathbf{r}_{v,f}(t) := V_f(t)\mathbf{r}_f(t)$, with $V_f(t)$ the volume of phase F and $\mathbf{r}_f(t)$ the R-dimensional vector of reaction rates in phase F, $\mathbf{u}_{in,f}(t)$ is the p_f-dimensional vector of inlet mass flowrates to phase F, $\omega_f(t) := \frac{u_{out,f}(t)}{m_f(t)}$ is the inverse of the residence time in phase F, with $u_{out,f}(t)$ the outlet mass flowrate from phase F and $m(t)$ the mass of phase F, $\mathbf{N}_f$ is the $R_f \times S_f$ stoichiometric matrix in phase F, $\mathbf{W}_{in,f}(t)$ is the $S_f \times p_f$ matrix of compositions of the inlets to phase F, whose jth column is $\mathbf{W}_{in,f,j}(t) := \mathbf{M}_{w,f}^{-1}\check{\mathbf{w}}_{in,f,j}(t)$, with $\mathbf{M}_{w,f}$ the S_f-dimensional diagonal matrix of molecular weights and $\check{\mathbf{w}}_{in,f,j}(t)$ the S_f-dimensional vector of weight fractions of the jth inlet to phase F, and $\mathbf{n}_{f,0}$ are the initial numbers of moles in phase F. Additionally, $\boldsymbol{\phi}_{m,f}^{v}(t) := V_f(t)\boldsymbol{\phi}_{m,f}(t)$, with $\boldsymbol{\phi}_{m,f}(t)$ the $p_{m,f}$-dimensional vector of molar mass-transfer rates per unit of volume describing the material transferred to phase F, and $\mathbf{E}_{m,f}$ is an $S_f \times p_{m,f}$ matrix with each row having one element equal to 1 if the corresponding species is transferred to phase F and the remaining elements equal to 0.

2.4.2 Heat balance equation, $Q_f(t)$

Let $\mathbf{c}_{p,f}(T,P)$ denote the S_f-dimensional vector of molar heat capacities at constant pressure, at the temperature T and pressure P, for the state of matter of phase F. Let us define the heat in phase F as

$$Q_f(t) := \bar{\mathbf{c}}_{p,f}(t)^{\mathrm{T}}\mathbf{n}_f(t)\left(T_f(t) - T_{ref}\right), \tag{2.64}$$

where $\bar{\mathbf{c}}_{p,f}(t) := \int_{T_{ref}}^{T_f(t)} \mathbf{c}_{p,f}(\theta, P_{ref})\mathrm{d}\theta / \left(T_f(t) - T_{ref}\right)$ is the S_f-dimensional vector of average molar heat capacities at constant pressure between $T_f(t)$ and T_{ref}, with $T_f(t)$ the temperature of phase F, and let us define the specific heats of the inlets to phase F as

$$\check{T}_{in,f,j}(t) := \bar{\mathbf{c}}_{p,in,f,j}(t)^{\mathrm{T}}\mathbf{W}_{in,f,j}(t)\left(T_{in,f,j}(t) - T_{ref}\right), \quad \forall j = 1,\ldots,p_f, \tag{2.65}$$

where $\bar{\mathbf{c}}_{p,in,f,j}(t) := \int_{T_{ref}}^{T_{in,f,j}(t)} \mathbf{c}_{p,f}(\theta, P_{ref})\mathrm{d}\theta / \left(T_{in,f,j}(t) - T_{ref}\right)$ is the S_f-dimensional vector of average molar heat capacities at constant pressure between $T_{in,f,j}(t)$ and T_{ref}, with $T_{in,f,j}(t)$ the temperature of the jth inlet to phase F.

Then, the heat balance for phase F can be expressed by the heat $Q_f(t)$ in phase F, which

is given by the ODE

$$\dot{Q}_f(t) = -\Delta\mathbf{H}_{r,f}^{\mathrm{T}}\mathbf{r}_{v,f}(t) - \Delta\mathbf{H}_{m,f}^{\mathrm{T}}\boldsymbol{\phi}_{m,f}^{v}(t) + q_{ex,f}(t) + \check{\mathbf{T}}_{in,f}(t)^{\mathrm{T}}\mathbf{u}_{in,f}(t) - \omega_f(t)Q_f(t),$$
$$Q_f(0) = Q_{f,0} := \bar{\mathbf{c}}_{p,f,0}^{\mathrm{T}}\mathbf{n}_{f,0}\left(T_{f,0} - T_{ref}\right), \tag{2.66}$$

where $\Delta\mathbf{H}_{r,f} := \mathbf{N}_f\Delta\mathbf{H}_f$ is the R_f-dimensional vector of enthalpies of reaction in phase F at T_{ref}, and $\Delta\mathbf{H}_{m,f} := \mathbf{E}_{m,f}^{\mathrm{T}}\Delta\mathbf{H}_f$ is the $p_{m,f}$-dimensional vector of enthalpies of mass transfer to phase F at T_{ref}, with $\Delta\mathbf{H}_f$ the S_f-dimensional vector of molar enthalpies of formation of the S_f species in phase F at the reference temperature T_{ref} and pressure P_{ref}. Note that $\Delta\mathbf{H}_{r,f}$ and $\Delta\mathbf{H}_{m,f}$ are constant, and $\check{\mathbf{T}}_{in,f}(t)$ is also constant if the composition and temperature of the inlets to phase F are constant.

Note that one can combine the material and heat balances by describing the system with the states $\mathbf{z}_f(t) := \begin{bmatrix}\mathbf{n}_f(t)\\ Q_f(t)\end{bmatrix}$.

2.5 Variants and Invariants for Homogeneous Reaction Systems

This section presents several transformations between original states related to the numbers of moles and a number of sets of variants and invariants. For the sake of simplicity, only the case of homogeneous lumped reactors is analyzed, and the heat balance is not considered. In the following section, a particular transformation, namely the transformation to extents, is detailed for lumped reaction systems with instantaneous equilibria, multiphase lumped reaction systems, and lumped reaction systems with heat balance.

2.5.1 Numbers of moles in variant and vessel-variant forms

Let us start by introducing some variables related to the numbers of moles, called numbers of moles in variant and vessel-variant forms, which are necessary for some of the transformations to variants and invariants. Then, the transformations between numbers of moles and related quantities and several sets of variants and invariants are presented.

2.5.1.1 Numbers of moles in reaction-variant form

The numbers of moles in reaction-variant form $\mathbf{n}^{RV}(t)$ represent the number of moles of all the species that have been processed by the reactions until time t. These numbers of moles in reaction-variant form are described by the ODE

$$\dot{\mathbf{n}}^{RV}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t), \qquad \mathbf{n}^{RV}(0) = \mathbf{0}_S, \tag{2.67}$$

and can be computed from the following equation, which results from integrating Eq. (2.19) and isolating the terms that depend on the reactions:

$$\mathbf{n}^{RV}(t) = \mathbf{n}(t) - \mathbf{n}_0 - \int_0^t \mathbf{W}_{in}(\tau)\mathbf{u}_{in}(\tau)\mathrm{d}\tau + \int_0^t \omega(\tau)\mathbf{n}(\tau)\mathrm{d}\tau. \tag{2.68}$$

The computation of the variables $\mathbf{n}^{RV}(t)$ requires knowledge of the inlet and outlet flowrates, inlet composition and initial conditions and integration of $\mathbf{n}(t)$.

2.5.1.2 Numbers of moles in reaction-flow-variant form

The numbers of moles in reaction-flow-variant form $\mathbf{n}^{RFV}(t)$ represent the number of moles of all the species that have been processed by the reactions or have flowed into the reactor via the inlets until time t. These numbers of moles in reaction-flow-variant form are described by the ODE

$$\dot{\mathbf{n}}^{RFV}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}(t)\mathbf{u}_{in}(t), \qquad \mathbf{n}^{RFV}(0) = \mathbf{0}_S, \tag{2.69}$$

and can be computed from the following equation, which results from integrating Eq. (2.19) and isolating the terms that depend on the reactions and inlet flows:

$$\mathbf{n}^{RFV}(t) = \mathbf{n}(t) - \mathbf{n}_0 + \int_0^t \omega(\tau)\mathbf{n}(\tau)\mathrm{d}\tau. \tag{2.70}$$

The computation of the variables $\mathbf{n}^{RFV}(t)$ requires knowledge of the outlet flowrate and initial conditions and integration of $\mathbf{n}(t)$ but no knowledge of the inlet flowrates and inlet composition.

2.5.1.3 Numbers of moles in vessel-reaction-variant form

The effect of the outlet flow on the initial and inlet flow conditions can be computed as $\mathbf{n}_{iic}(t)$ by solving the ODE

$$\dot{\mathbf{n}}_{iic}(t) = \mathbf{W}_{in}(t)\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}_{iic}(t), \qquad \mathbf{n}_{iic}(0) = \mathbf{n}_0. \tag{2.71}$$

The numbers of moles in vessel-reaction-variant form $\mathbf{n}^{vRV}(t)$ represent the number of moles of all the species that have been processed by the reactions and are in the vessel at time t, that is, discounting for the amount that has left the vessel via the outlet. These numbers of moles in vessel-reaction-variant form are described by the ODE

$$\dot{\mathbf{n}}^{vRV}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) - \omega(t)\mathbf{n}^{vRV}(t), \qquad \mathbf{n}^{vRV}(0) = \mathbf{0}_S, \tag{2.72}$$

and can be computed from the following equation, which results from Eqs. (2.19) and

(2.71):

$$\mathbf{n}^{vRV}(t) = \mathbf{n}(t) - \mathbf{n}_{iic}(t). \tag{2.73}$$

The computation of the variables $\mathbf{n}_{iic}(t)$ and $\mathbf{n}^{vRV}(t)$ requires knowledge of the inlet and outlet flowrates, inlet composition and initial conditions but no integration of $\mathbf{n}(t)$. Note that, in batch and semi-batch homogeneous reactors, $\mathbf{n}^{RV}(t)$ and $\mathbf{n}^{vRV}(t)$ are equal, and no integration of $\mathbf{n}(t)$ is necessary to compute them.

2.5.1.4 Numbers of moles in vessel-reaction-flow-variant form

The effect of the outlet flow on the initial conditions can be computed as $\mathbf{n}_{ic}(t)$ by solving the ODE

$$\dot{\mathbf{n}}_{ic}(t) = -\omega(t)\mathbf{n}_{ic}(t), \qquad \mathbf{n}_{ic}(0) = \mathbf{n}_0. \tag{2.74}$$

The numbers of moles in vessel-reaction-flow-variant form $\mathbf{n}^{vRFV}(t)$ represent the number of moles of all the species that have been processed by the reactions or have flowed into the reactor via the inlets and are in the vessel at time t, that is, discounting for the amount that has left the vessel via the outlet. These numbers of moles in vessel-reaction-flow-variant form are described by the ODE

$$\dot{\mathbf{n}}^{vRFV}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}(t)\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}^{vRFV}(t), \qquad \mathbf{n}^{vRFV}(0) = \mathbf{0}_S, \tag{2.75}$$

and can be computed from the following equation, which results from Eqs. (2.19) and (2.74):

$$\mathbf{n}^{vRFV}(t) = \mathbf{n}(t) - \mathbf{n}_{ic}(t). \tag{2.76}$$

The computation of the variables $\mathbf{n}_{ic}(t)$ and $\mathbf{n}^{vRFV}(t)$ requires knowledge of the outlet flowrate and initial conditions but no knowledge of the inlet flowrates and inlet composition and no integration of $\mathbf{n}(t)$. Note that, in batch and semi-batch homogeneous reactors, $\mathbf{n}^{RFV}(t)$ and $\mathbf{n}^{vRFV}(t)$ are equal, and no integration of $\mathbf{n}(t)$ is necessary to compute them. Furthermore, in batch homogeneous reactors, all the variables $\mathbf{n}^{RV}(t)$, $\mathbf{n}^{RFV}(t)$, $\mathbf{n}^{vRV}(t)$ and $\mathbf{n}^{vRFV}(t)$ are equal.

2.5.2 From numbers of moles to reaction variants and invariants

2.5.2.1 Reaction variants and invariants $\mathbf{y}_r(t)$ and $\mathbf{y}_{iv}(t)$

The reaction variant $y_{r,i}(t)$ represents an abstract variable that is influenced by the ith reaction but not by the other reactions. These variants are described by the ODE

$$\dot{\mathbf{y}}_r(t) = \mathbf{r}_v(t) + \mathscr{L}^+\mathbf{W}_{in}(t)\mathbf{u}_{in}(t) - \omega(t)\mathbf{y}_r(t), \qquad \mathbf{y}_r(0) = \mathscr{L}^+\mathbf{n}_0, \tag{2.77}$$

where $\mathscr{L}^+$ is the Moore-Penrose pseudoinverse of $\mathscr{L}$, with $\mathscr{L} = \mathbf{N}^{\mathrm{T}}$. However, $\mathbf{y}_r(t)$ are not pure reaction variants in the presence of inlets since they are also flow variants, that is, influenced by the inlet flows.

Let us assume that rank $\left(\mathbf{N}^{\mathrm{T}}\right) = R$, which can always be achieved via appropriate choice of the stoichiometries and reaction rates according to the results in Section 2.1. Since rank $\left(\mathbf{N}^{\mathrm{T}}\right) = R$, the null space of $\mathscr{L}^{\mathrm{T}}$ is of dimension $q := S - R$ and is described by the $S \times q$ matrix $\mathbf{P}$, that is, $\mathscr{L}^{\mathrm{T}}\mathbf{P} = \mathbf{0}_{R\times q}$. The q reaction invariants $\mathbf{y}_{iv}(t)$ represent abstract variables that are not influenced by the reactions. These invariants are described by the ODE

$$\dot{\mathbf{y}}_{iv}(t) = \mathbf{P}^+\mathbf{W}_{in}(t)\mathbf{u}_{in}(t) - \omega(t)\mathbf{y}_{iv}(t), \qquad \mathbf{y}_{iv}(0) = \mathbf{P}^+\mathbf{n}_0, \tag{2.78}$$

where $\mathbf{P}^+$ is the Moore-Penrose pseudoinverse of $\mathbf{P}$. However, $\mathbf{y}_{iv}(t)$ are not true invariants in the presence of inlets since they are also flow variants, that is, influenced by the inlet flows.

Since rank$(\mathscr{L}) = R$, Eq. (2.19) can be reconstructed from Eqs. (2.77) and (2.78) using

$$\mathbf{n}(t) = \begin{bmatrix}\mathscr{L} & \mathbf{P}\end{bmatrix}\begin{bmatrix}\mathbf{y}_r(t)\\ \mathbf{y}_{iv}(t)\end{bmatrix}. \tag{2.79}$$

2.5.2.2 Transformation to variants and invariants

The reaction variants $\mathbf{y}_r$ and the reaction invariants $\mathbf{y}_{iv}$ can be computed from the numbers of moles $\mathbf{n}$ by inversion of Eq. (2.79). The reaction variants are given by the linear transformation

$$\mathbf{y}_r(t) = \mathscr{L}^+\mathbf{n}(t), \tag{2.80}$$

whereas the reaction invariants are given by the linear transformation

$$\mathbf{y}_{iv}(t) = \mathbf{P}^+\mathbf{n}(t). \tag{2.81}$$

The computation of the variables $\mathbf{y}_r(t)$ and $\mathbf{y}_{iv}(t)$ via linear transformation requires no knowledge of the inlet and outlet flowrates, inlet composition and initial conditions and no integration of $\mathbf{n}(t)$, but it does not allow obtaining pure reaction variants or true invariants.

2.5.3 From numbers of moles to reaction and inlet variants and invariants

2.5.3.1 Reaction and inlet variants and invariants $\mathbf{z}_r(t)$, $\mathbf{z}_{in}(t)$ and $\mathbf{z}_{iv}(t)$

Let us assume that the inlet composition given by $\mathbf{W}_{in}(t)$ is constant. The reaction variant $z_{r,i}(t)$ represents an abstract variable that is influenced by the ith reaction but not by the other reactions or by the inlet flows, while the inlet variant $z_{in,j}(t)$ represents an abstract variable that is influenced by the jth inlet flow but not by the other inlet flows or by the reactions. These variants are described by the ODE

$$\begin{bmatrix} \dot{\mathbf{z}}_r(t) \\ \dot{\mathbf{z}}_{in}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{r}_v(t) \\ \mathbf{u}_{in}(t) \end{bmatrix} - \omega(t) \begin{bmatrix} \mathbf{z}_r(t) \\ \mathbf{z}_{in}(t) \end{bmatrix}, \qquad \begin{bmatrix} \mathbf{z}_r(0) \\ \mathbf{z}_{in}(0) \end{bmatrix} = \mathscr{L}^+ \mathbf{n}_0, \tag{2.82}$$

where $\mathscr{L}^+$ is the Moore-Penrose pseudoinverse of $\mathscr{L}$, with $\mathscr{L} = \begin{bmatrix} \mathbf{N}^{\mathrm{T}} & \mathbf{W}_{in} \end{bmatrix}$. Now $\mathbf{z}_r(t)$ are pure reaction variants and flow invariants, while $\mathbf{z}_{in}(t)$ are pure flow variants and reaction invariants.

Let us also assume that $\operatorname{rank}\left(\begin{bmatrix} \mathbf{N}^{\mathrm{T}} & \mathbf{W}_{in} \end{bmatrix}\right) = R + p$. Then, the null space of $\mathscr{L}^{\mathrm{T}}$ is of dimension $q := S - R - p$ and is described by the $S \times q$ matrix $\mathbf{P}$, that is, $\mathscr{L}^{\mathrm{T}}\mathbf{P} = \mathbf{0}_{(R+p)\times q}$. The q reaction invariants $\mathbf{z}_{iv}(t)$ represent abstract variables that are influenced neither by the reactions nor by the inlet flows. These invariants are described by the ODE

$$\dot{\mathbf{z}}_{iv}(t) = -\omega(t)\mathbf{z}_{iv}(t), \qquad \mathbf{z}_{iv}(0) = \mathbf{P}^+ \mathbf{n}_0, \tag{2.83}$$

where $\mathbf{P}^+$ is the Moore-Penrose pseudoinverse of $\mathbf{P}$. Now $\mathbf{z}_{iv}(t)$ are reaction and flow invariants, although they are not true invariants.

Since $\operatorname{rank}(\mathscr{L}) = R + p$, Eq. (2.19) can be reconstructed from Eqs. (2.82) and (2.83) using

$$\mathbf{n}(t) = \begin{bmatrix} \mathscr{L} & \mathbf{P} \end{bmatrix} \begin{bmatrix} \mathbf{z}_r(t) \\ \mathbf{z}_{in}(t) \\ \mathbf{z}_{iv}(t) \end{bmatrix}. \tag{2.84}$$

2.5.3.2 Transformation to variants and invariants

The reaction variants $\mathbf{z}_r$, the flow variants $\mathbf{z}_{in}$ and the reaction and flow invariants $\mathbf{z}_{iv}$ can be computed from the numbers of moles $\mathbf{n}$ by inversion of Eq. (2.84). The reaction variants and the flow variants are given by the linear transformation

$$\begin{bmatrix} \mathbf{z}_r(t) \\ \mathbf{z}_{in}(t) \end{bmatrix} = \mathscr{L}^+ \mathbf{n}(t), \tag{2.85}$$

whereas the reaction and flow invariants are given by the linear transformation

$$\mathbf{z}_{iv}(t) = \mathbf{P}^{+}\mathbf{n}(t). \tag{2.86}$$

The computation of the variables $\mathbf{z}_r(t)$, $\mathbf{z}_{in}(t)$ and $\mathbf{z}_{iv}(t)$ via linear transformation requires knowledge of the inlet composition but no knowledge of the inlet and outlet flowrates and initial conditions and no integration of $\mathbf{n}(t)$, and it allows obtaining pure reaction and inlet variants but it does not allow obtaining true invariants.

2.5.4 From numbers of moles in reaction-variant form to batch extents

2.5.4.1 Batch extents $\xi_r(t)$

The batch extent of reaction $\xi_{r,i}(t)$ represents the amount of material that has been processed by the ith reaction until time t. These batch extents are described by the ODE

$$\dot{\xi}_r(t) = \mathbf{r}_v(t), \qquad \xi_r(0) = \mathbf{0}_R. \tag{2.87}$$

Eq. (2.19) can be reconstructed from Eq. (2.87) using

$$\mathbf{n}(t) = \mathscr{L}\xi_r(t) + \mathbf{n}_0 + \int_0^t \mathbf{W}_{in}(\tau)\mathbf{u}_{in}(\tau)\mathrm{d}\tau - \int_0^t \omega(\tau)\mathbf{n}(\tau)\mathrm{d}\tau, \tag{2.88}$$

with $\mathscr{L} = \mathbf{N}^{\mathrm{T}}$.

2.5.4.2 Transformation to batch extents

The batch extents ξ_r can be computed from the numbers of moles $\mathbf{n}$ by inversion of Eq. (2.88). If $\mathrm{rank}(\mathscr{L}) = R$, then $\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}$ is invertible for any positive definite weighting matrix $\mathbf{W}$ of dimension S, and the batch extents are given by the linear transformation

$$\xi_r(t) = \mathscr{T}\mathbf{n}^{RV}(t), \tag{2.89}$$

with $\mathscr{T} := \left(\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}\right)^{-1}\mathscr{L}^{\mathrm{T}}\mathbf{W}$ and $\mathbf{n}^{RV}(t)$ given by Eq. (2.68).

2.5.4.3 Transformation to invariants

The null space of $\mathscr{L}^{\mathrm{T}}$ is of dimension $q := S - \mathrm{rank}(\mathscr{L})$ and is described by the $S \times q$ matrix $\mathbf{P}$, that is, $\mathscr{L}^{\mathrm{T}}\mathbf{P} = \mathbf{0}_{R\times q}$. Then, the q invariants $\xi_{iv}(t) = \mathbf{0}_q$ are given by the linear transformation

$$\xi_{iv}(t) = \mathbf{P}^{\mathrm{T}}\mathbf{n}^{RV}(t). \tag{2.90}$$

The computation of the variables $\xi_r(t)$ and $\xi_{iv}(t)$ via linear transformation requires knowledge of the inlet and outlet flowrates, inlet composition and initial conditions and integration of $\mathbf{n}(t)$, and allows obtaining pure reaction variants and at least $S-R$ invariants.

2.5.5 From numbers of moles in reaction-flow-variant form to batch extents

2.5.5.1 Batch extents $\xi_r(t)$ and $\xi_{in}(t)$

The batch extents of reaction $\xi_r(t)$ are described by Eq. (2.87).

The batch extent of inlet $\xi_{in,j}(t)$ represents the amount of material that has flowed into the reactor via the jth inlet until time t. These batch extents are described by the ODE

$$\dot{\xi}_{in}(t) = \mathbf{u}_{in}(t), \qquad \xi_{in}(0) = \mathbf{0}_p. \tag{2.91}$$

Let us assume that the inlet composition given by $\mathbf{W}_{in}(t)$ is constant. Eq. (2.19) can be reconstructed from Eqs. (2.87) and (2.91) using

$$\mathbf{n}(t) = \mathscr{L}\begin{bmatrix}\xi_r(t)\\ \xi_{in}(t)\end{bmatrix} + \mathbf{n}_0 - \int_0^t \omega(\tau)\mathbf{n}(\tau)\mathrm{d}\tau, \tag{2.92}$$

with $\mathscr{L} = \begin{bmatrix}\mathbf{N}^{\mathrm{T}} & \mathbf{W}_{in}\end{bmatrix}$.

2.5.5.2 Transformation to batch extents

The batch extents ξ_r and ξ_{in} can be computed from the numbers of moles $\mathbf{n}$ by inversion of Eq. (2.92). If $\mathrm{rank}(\mathscr{L}) = R+p$, then $\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}$ is invertible for any positive definite weighting matrix $\mathbf{W}$ of dimension S, and the batch extents are given by the linear transformation

$$\begin{bmatrix}\xi_r(t)\\ \xi_{in}(t)\end{bmatrix} = \mathscr{T}\mathbf{n}^{RFV}(t), \tag{2.93}$$

with $\mathscr{T} := \left(\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}\right)^{-1}\mathscr{L}^{\mathrm{T}}\mathbf{W}$ and $\mathbf{n}^{RFV}(t)$ given by Eq. (2.70).

2.5.5.3 Transformation to invariants

The null space of $\mathscr{L}^{\mathrm{T}}$ is of dimension $q := S - \mathrm{rank}(\mathscr{L})$ and is described by the $S \times q$ matrix $\mathbf{P}$, that is, $\mathscr{L}^{\mathrm{T}}\mathbf{P} = \mathbf{0}_{(R+p)\times q}$. Then, the q invariants $\xi_{iv}(t) = \mathbf{0}_q$ are given by the linear transformation

$$\xi_{iv}(t) = \mathbf{P}^{\mathrm{T}}\mathbf{n}^{RFV}(t). \tag{2.94}$$

The computation of the variables $\xi_r(t)$, $\xi_{in}(t)$ and $\xi_{iv}(t)$ via linear transformation re-

quires knowledge of the outlet flowrate, inlet composition and initial conditions and integration of $\mathbf{n}(t)$ but no knowledge of the inlet flowrates, and allows obtaining pure reaction and inlet variants and at least $S-R-p$ invariants.

2.5.6 From numbers of moles in vessel-reaction-variant form to vessel extents

2.5.6.1 Vessel extents $\mathbf{x}_r(t)$

The vessel extent of reaction $x_{r,i}(t)$ represents the amount of material that has been processed by the ith reaction and is in the vessel at time t, that is, discounting for the amount that has left the vessel via the outlet. These vessel extents are described by the ODE

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t), \qquad \mathbf{x}_r(0) = \mathbf{0}_R. \tag{2.95}$$

Eq. (2.19) can be reconstructed from Eq. (2.95) using

$$\mathbf{n}(t) = \mathscr{L}\mathbf{x}_r(t) + \mathbf{n}_{iic}(t), \tag{2.96}$$

with $\mathscr{L} = \mathbf{N}^{\mathrm{T}}$.

2.5.6.2 Transformation to vessel extents

The vessel extents $\mathbf{x}_r$ can be computed from the numbers of moles $\mathbf{n}$ by inversion of Eq. (2.96). If $\mathrm{rank}(\mathscr{L}) = R$, then $\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}$ is invertible for any positive definite weighting matrix $\mathbf{W}$ of dimension S, and the vessel extents are given by the linear transformation

$$\mathbf{x}_r(t) = \mathscr{T}\mathbf{n}^{\nu RV}(t), \tag{2.97}$$

with $\mathscr{T} := \left(\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}\right)^{-1}\mathscr{L}^{\mathrm{T}}\mathbf{W}$ and $\mathbf{n}^{\nu RV}(t)$ given by Eq. (2.72).

2.5.6.3 Transformation to invariants

The null space of $\mathscr{L}^{\mathrm{T}}$ is of dimension $q := S - \mathrm{rank}(\mathscr{L})$ and is described by the $S \times q$ matrix $\mathbf{P}$, that is, $\mathscr{L}^{\mathrm{T}}\mathbf{P} = \mathbf{0}_{R\times q}$. Then, the q invariants $\mathbf{x}_{iv}(t) = \mathbf{0}_q$ are given by the linear transformation

$$\mathbf{x}_{iv}(t) = \mathbf{P}^{\mathrm{T}}\mathbf{n}^{\nu RV}(t). \tag{2.98}$$

The computation of the variables $\mathbf{x}_r(t)$ and $\mathbf{x}_{iv}(t)$ via linear transformation requires knowledge of the inlet and outlet flowrates, inlet composition and initial conditions but no integration of $\mathbf{n}(t)$, and allows obtaining pure reaction variants and at least $S-R$ invariants.

Since $\mathbf{n}^{RV}(t)$ and $\mathbf{n}^{\nu RV}(t)$ are equal in batch and semi-batch homogeneous reactors, the batch extents $\boldsymbol{\xi}_r(t)$ and the invariants $\boldsymbol{\xi}_{iv}(t)$ are equal to the vessel extents $\mathbf{x}_r(t)$ and the

invariants $\mathbf{x}_{iv}(t)$ in these reactors.

2.5.7 From numbers of moles in vessel-reaction-flow-variant form to vessel extents

2.5.7.1 Vessel extents $\mathbf{x}_r(t)$ and $\mathbf{x}_{in}(t)$

The vessel extents of reaction $\mathbf{x}_r(t)$ are described by Eq. (2.95).

The vessel extent of inlet $x_{in,j}(t)$ represents the amount of material that has flowed into the reactor via the jth inlet and is in the vessel at time t, that is, discounting for the amount that has left the vessel via the outlet. These vessel extents are described by the ODE

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) - \omega(t)\mathbf{x}_{in}(t), \qquad \mathbf{x}_{in}(0) = \mathbf{0}_p. \tag{2.99}$$

Let us assume that the inlet composition given by $\mathbf{W}_{in}(t)$ is constant. Eq. (2.19) can be reconstructed from Eqs. (2.95) and (2.99) using

$$\mathbf{n}(t) = \mathscr{L}\begin{bmatrix}\mathbf{x}_r(t)\\ \mathbf{x}_{in}(t)\end{bmatrix} + \mathbf{n}_{ic}(t), \tag{2.100}$$

with $\mathscr{L} = \begin{bmatrix}\mathbf{N}^{\mathrm{T}} & \mathbf{W}_{in}\end{bmatrix}$.

2.5.7.2 Transformation to vessel extents

The vessel extents $\mathbf{x}_r$ and $\mathbf{x}_{in}$ can be computed from the numbers of moles $\mathbf{n}$ by inversion of Eq. (2.100). If $\operatorname{rank}(\mathscr{L}) = R + p$, then $\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}$ is invertible for any positive definite weighting matrix $\mathbf{W}$ of dimension S, and the vessel extents are given by the linear transformation

$$\begin{bmatrix}\mathbf{x}_r(t)\\ \mathbf{x}_{in}(t)\end{bmatrix} = \mathscr{T}\mathbf{n}^{vRFV}(t), \tag{2.101}$$

with $\mathscr{T} := \left(\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}\right)^{-1}\mathscr{L}^{\mathrm{T}}\mathbf{W}$ and $\mathbf{n}^{vRFV}(t)$ given by Eq. (2.75).

2.5.7.3 Transformation to invariants

The null space of $\mathscr{L}^{\mathrm{T}}$ is of dimension $q := S - \operatorname{rank}(\mathscr{L})$ and is described by the $S \times q$ matrix $\mathbf{P}$, that is, $\mathscr{L}^{\mathrm{T}}\mathbf{P} = \mathbf{0}_{(R+p)\times q}$. Then, the q invariants $\mathbf{x}_{iv}(t) = \mathbf{0}_q$ are given by the linear transformation

$$\mathbf{x}_{iv}(t) = \mathbf{P}^{\mathrm{T}}\mathbf{n}^{vRFV}(t). \tag{2.102}$$

The computation of the variables $\mathbf{x}_r(t)$, $\mathbf{x}_{in}(t)$ and $\mathbf{x}_{iv}(t)$ via linear transformation re-

quires knowledge of the outlet flowrate, inlet composition and initial conditions but no knowledge of the inlet flowrates and no integration of $\mathbf{n}(t)$, and allows obtaining pure reaction and inlet variants and at least $S-R-p$ invariants.

Since $\mathbf{n}^{RFV}(t)$ and $\mathbf{n}^{vRFV}(t)$ are equal in batch and semi-batch homogeneous reactors, the batch extents $\boldsymbol{\xi}_r(t)$ and $\boldsymbol{\xi}_{in}(t)$ and the invariants $\boldsymbol{\xi}_{iv}(t)$ are equal to the vessel extents $\mathbf{x}_r(t)$ and $\mathbf{x}_{in}(t)$ and the invariants $\mathbf{x}_{iv}(t)$ in these reactors.

2.5.8 From numbers of moles to vessel extents

2.5.8.1 Vessel extents $\mathbf{x}_r(t)$, $\mathbf{x}_{in}(t)$ and $x_{ic}(t)$

The vessel extents of reaction $\mathbf{x}_r(t)$ and the vessel extents of inlet $\mathbf{x}_{in}(t)$ are described by Eqs. (2.95) and (2.99).

The vessel extent of initial conditions $x_{ic}(t)$ represents the amount of material that was initially in the reactor and is in the vessel at time t, that is, discounting for the amount that has left the vessel via the outlet. This vessel extent is described by the ODE

$$\dot{x}_{ic}(t) = -\omega(t)x_{ic}(t), \qquad x_{ic}(0) = 1. \tag{2.103}$$

Note that, in batch and semi-batch homogeneous reactors, the vessel extent of initial conditions $x_{ic}(t)$ is simply given by

$$x_{ic}(t) = 1. \tag{2.104}$$

Let us assume that the inlet composition given by $\mathbf{W}_{in}(t)$ is constant. Eq. (2.19) can be reconstructed from Eqs. (2.95), (2.99) and (2.103) using

$$\mathbf{n}(t) = \mathscr{L} \begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \end{bmatrix}, \tag{2.105}$$

with $\mathscr{L} = \begin{bmatrix} \mathbf{N}^{\mathrm{T}} & \mathbf{W}_{in} & \mathbf{n}_0 \end{bmatrix}$. Note that this implies that the S numbers of moles $\mathbf{n}(t)$ can be computed as a linear transformation of $R+p+1$ vessel extents.

Furthermore, from Eqs. (2.96), (2.100) and (2.105), it is possible to show the following relationships:

$$\mathbf{n}_{iic}(t) = \mathbf{W}_{in}\mathbf{x}_{in}(t) + \mathbf{n}_0 x_{ic}(t), \tag{2.106}$$

$$\mathbf{n}_{ic}(t) = \mathbf{n}_0 x_{ic}(t). \tag{2.107}$$

2.5.8.2 Transformation to vessel extents

The vessel extents $\mathbf{x}_r$, $\mathbf{x}_{in}$ and x_{ic} can be computed from the numbers of moles $\mathbf{n}$ by inversion of Eq. (2.105). If $\operatorname{rank}(\mathscr{L}) = R + p + 1$, then $\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}$ is invertible for any positive definite weighting matrix $\mathbf{W}$ of dimension S, and the vessel extents are given by the linear transformation

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \end{bmatrix} = \mathscr{T}\mathbf{n}(t), \tag{2.108}$$

with $\mathscr{T} := \left(\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}\right)^{-1}\mathscr{L}^{\mathrm{T}}\mathbf{W}$.

2.5.8.3 Transformation to invariants

The null space of $\mathscr{L}^{\mathrm{T}}$ is of dimension $q := S - \operatorname{rank}(\mathscr{L})$ and is described by the $S \times q$ matrix $\mathbf{P}$, that is, $\mathscr{L}^{\mathrm{T}}\mathbf{P} = \mathbf{0}_{(R+p+1)\times q}$. Then, the q invariants $\mathbf{x}_{iv}(t) = \mathbf{0}_q$ are given by the linear transformation

$$\mathbf{x}_{iv}(t) = \mathbf{P}^{\mathrm{T}}\mathbf{n}(t). \tag{2.109}$$

The computation of the variables $\mathbf{x}_r(t)$, $\mathbf{x}_{in}(t)$, $x_{ic}(t)$ and $\mathbf{x}_{iv}(t)$ via linear transformation requires knowledge of the inlet composition and initial conditions but no knowledge of the inlet and outlet flowrates and no integration of $\mathbf{n}(t)$, and allows obtaining pure reaction and inlet variants and at least $S - R - p - 1$ invariants.

2.5.9 From numbers of moles to extents in batch homogeneous reactors

2.5.9.1 Extents $\mathbf{x}_r(t)$

In batch homogeneous reactors, Eq. (2.45) can be reconstructed from Eq. (2.95) using

$$\mathbf{n}(t) = \mathscr{L}\mathbf{x}_r(t) + \mathbf{n}_0, \tag{2.110}$$

with $\mathscr{L} = \mathbf{N}^{\mathrm{T}}$. Note that this implies that the S numbers of moles $\mathbf{n}(t)$ can be computed as a linear transformation of R extents.

In these reactors, since $p = 0$ and $\omega(t) = 0$,

$$\mathbf{n}_{iic}(t) = \mathbf{n}_0 + \int_0^t \mathbf{W}_{in}(\tau)\mathbf{u}_{in}(\tau)\mathrm{d}\tau - \int_0^t \omega(\tau)\mathbf{n}(\tau)\mathrm{d}\tau = \mathbf{n}_0, \tag{2.111}$$

$$\mathbf{n}^{RV}(t) = \mathbf{n}^{vRV}(t) = \mathbf{n}(t) - \mathbf{n}_0, \tag{2.112}$$

which implies that Eq. (2.110) is equivalent to Eqs. (2.88) and (2.96).

2.5.9.2 Transformation to extents

The (batch) extents $\mathbf{x}_r$ can be computed from the numbers of moles $\mathbf{n}$ by inversion of Eq. (2.110). If $\text{rank}(\mathscr{L}) = R$, then $\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}$ is invertible for any positive definite weighting matrix $\mathbf{W}$ of dimension S, and the extents are given by the linear transformation

$$\mathbf{x}_r(t) = \mathscr{T}\left(\mathbf{n}(t) - \mathbf{n}_0\right), \tag{2.113}$$

with $\mathscr{T} := \left(\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}\right)^{-1}\mathscr{L}^{\mathrm{T}}\mathbf{W}$.

2.5.9.3 Transformation to invariants

The null space of $\mathscr{L}^{\mathrm{T}}$ is of dimension $q := S - \text{rank}(\mathscr{L})$ and is described by the $S \times q$ matrix $\mathbf{P}$, that is, $\mathscr{L}^{\mathrm{T}}\mathbf{P} = \mathbf{0}_{R\times q}$. Then, the q invariants $\mathbf{x}_{iv}(t) = \mathbf{0}_q$ are given by the linear transformation

$$\mathbf{x}_{iv}(t) = \mathbf{P}^{\mathrm{T}}\left(\mathbf{n}(t) - \mathbf{n}_0\right). \tag{2.114}$$

The computation of the variables $\mathbf{x}_r(t)$ and $\mathbf{x}_{iv}(t)$ via linear transformation requires knowledge of the initial conditions but no integration of $\mathbf{n}(t)$, and allows obtaining pure reaction variants and at least $S - R$ invariants.

2.5.10 From numbers of moles to extents in semi-batch homogeneous reactors

2.5.10.1 Extents $\mathbf{x}_r(t)$ and $\mathbf{x}_{in}(t)$

In semi-batch homogeneous reactors, Eq. (2.47) can be reconstructed from Eqs. (2.95) and (2.99) using

$$\mathbf{n}(t) = \mathscr{L}\begin{bmatrix}\mathbf{x}_r(t)\\ \mathbf{x}_{in}(t)\end{bmatrix} + \mathbf{n}_0, \tag{2.115}$$

with $\mathscr{L} = \begin{bmatrix}\mathbf{N}^{\mathrm{T}} & \mathbf{W}_{in}\end{bmatrix}$. Note that this implies that the S numbers of moles $\mathbf{n}(t)$ can be computed as a linear transformation of $R + p$ extents.

In these reactors, since $\omega(t) = 0$,

$$\mathbf{n}_{ic}(t) = \mathbf{n}_0 - \int_0^t \omega(\tau)\mathbf{n}(\tau)\mathrm{d}\tau = \mathbf{n}_0, \tag{2.116}$$

$$\mathbf{n}^{RFV}(t) = \mathbf{n}^{\nu RFV}(t) = \mathbf{n}(t) - \mathbf{n}_0, \tag{2.117}$$

which implies that Eq. (2.115) is equivalent to Eqs. (2.92) and (2.100).

2.5.10.2 Transformation to extents

The (batch) extents $\mathbf{x}_r$ and $\mathbf{x}_{in}$ can be computed from the numbers of moles $\mathbf{n}$ by inversion of Eq. (2.115). If $\text{rank}(\mathscr{L}) = R + p$, then $\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}$ is invertible for any positive definite weighting matrix $\mathbf{W}$ of dimension S, and the extents are given by the linear transformation

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{in}(t) \end{bmatrix} = \mathscr{T}\left(\mathbf{n}(t) - \mathbf{n}_0\right), \tag{2.118}$$

with $\mathscr{T} := \left(\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}\right)^{-1}\mathscr{L}^{\mathrm{T}}\mathbf{W}$.

2.5.10.3 Transformation to invariants

The null space of $\mathscr{L}^{\mathrm{T}}$ is of dimension $q := S - \text{rank}(\mathscr{L})$ and is described by the $S \times q$ matrix $\mathbf{P}$, that is, $\mathscr{L}^{\mathrm{T}}\mathbf{P} = \mathbf{0}_{(R+p)\times q}$. Then, the q invariants $\mathbf{x}_{iv}(t) = \mathbf{0}_q$ are given by the linear transformation

$$\mathbf{x}_{iv}(t) = \mathbf{P}^{\mathrm{T}}\left(\mathbf{n}(t) - \mathbf{n}_0\right). \tag{2.119}$$

The computation of the variables $\mathbf{x}_r(t)$, $\mathbf{x}_{in}(t)$ and $\mathbf{x}_{iv}(t)$ via linear transformation requires knowledge of the inlet composition and initial conditions but no knowledge of the inlet flowrates and no integration of $\mathbf{n}(t)$, and allows obtaining pure reaction and inlet variants and at least $S - R - p$ invariants.

2.5.11 From numbers of moles to vessel extents in particular cases of open homogeneous reactors

As mentioned before, the numbers of moles can be computed as a linear transformation of $R + p + 1$ vessel extents in the general case of homogeneous reaction systems, R extents in batch homogeneous reactors, and $R + p$ extents in semi-batch homogeneous reactors. However, as shown in Appendix A.3, the numbers of moles can be computed as a linear transformation of less than $R + p + 1$ vessel extents in some particular cases of open homogeneous reactors.

These particular cases are the following: if (i) the initial conditions are a linear combination of the stoichiometries and of the inlet compositions, only $R + p$ vessel extents are needed; if (ii) the inverse of the residence time is a linear combination of reaction rates and inlet flowrates, only $R + p$ vessel extents are needed; and if both (i) and (ii) hold, only $R + p - 1$ vessel extents are needed. For example, if the initial conditions correspond to a steady state, then condition (i) is satisfied; if the reactor is a homogeneous continuous stirred-tank reactor (CSTR), which is an open homogeneous reactor with constant volume, and the reactor contains a mixture with constant density or an ideal mixture (such that the volume of the mixture is the sum of the volumes of each pure species), then condition (ii)

is satisfied.

The linear transformations from vessel extents to numbers of moles for each case are also shown in Appendix A.3. From these linear transformations, it is possible to obtain linear transformations from numbers of moles to vessel extents and to invariants as presented throughout this section.

2.5.12 From measured quantities to reconciled quantities

Let the vector $\delta\mathbf{n}$ of dimension S denote one of the quantities related to the numbers of moles that has been presented in the previous sections, and let $\delta\tilde{\mathbf{n}}$ be the corresponding measured data, corrupted by zero-mean noise with variance-covariance matrix $\boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}$. Then, let us consider the problem of reconciling the measured data, which is an optimization problem with the reconciled data $\delta\hat{\mathbf{n}}$ as decision variables, written as follows:[2]

$$\begin{aligned} \min_{\delta\hat{\mathbf{n}}} \quad & J_c(\delta\hat{\mathbf{n}}) = (\delta\hat{\mathbf{n}} - \delta\tilde{\mathbf{n}})^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} (\delta\hat{\mathbf{n}} - \delta\tilde{\mathbf{n}}) \\ & \qquad = \delta\hat{\mathbf{n}}^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} \delta\hat{\mathbf{n}} - 2\delta\hat{\mathbf{n}}^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} \delta\tilde{\mathbf{n}} + \delta\tilde{\mathbf{n}}^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} \delta\tilde{\mathbf{n}} \\ \text{s.t.} \quad & \mathbf{P}^{\mathrm{T}} \delta\hat{\mathbf{n}} = \mathbf{0}_q. \end{aligned} \tag{2.120}$$

The measured data $\delta\tilde{\mathbf{n}}$ are reconciled due to invariant linear equality constraints on the reconciled data $\delta\hat{\mathbf{n}}$. The columns of the $S \times q$ matrix $\mathbf{P}$ that specifies these constraints are a basis of the null space of the $(S-q) \times S$ matrix $\boldsymbol{\mathscr{L}}^{\mathrm{T}}$ of rank $S-q$, as expressed by

$$\boldsymbol{\mathscr{L}}^{\mathrm{T}} \mathbf{P} = \mathbf{0}_{(S-q)\times q}. \tag{2.121}$$

This is equivalent to saying that the columns of $\boldsymbol{\mathscr{L}}$ are a basis of the null space of $\mathbf{P}^{\mathrm{T}}$, that is

$$\mathbf{P}^{\mathrm{T}} \boldsymbol{\mathscr{L}} = \mathbf{0}_{q\times(S-q)}. \tag{2.122}$$

It is known that any optimization problem with decision variables $\delta\hat{\mathbf{n}}$ and constrained by the linear equality constraints $\mathbf{A}\delta\hat{\mathbf{n}} = \mathbf{b}$ can be converted to an equivalent optimization problem, in which these constraints are discarded and $\delta\hat{\mathbf{n}}$ is replaced by $\delta\hat{\mathbf{n}}_s + \mathbf{F}\hat{\mathbf{x}}$, where $\hat{\mathbf{x}}$ are the new decision variables, $\delta\hat{\mathbf{n}}_s$ is a particular solution of $\mathbf{A}\delta\hat{\mathbf{n}} = \mathbf{b}$ and the columns of $\mathbf{F}$ are a basis of the null space of $\mathbf{A}$ (for example, see [80], p. 132).

In the particular case of reconciliation of measured numbers of moles, one can observe that the variables $\hat{\mathbf{x}}$ represent variants, namely batch extents or vessel extents. Furthermore, for the linear equality constraints $\mathbf{P}^{\mathrm{T}}\delta\hat{\mathbf{n}} = \mathbf{0}_q$, it is clear that $\mathbf{0}_S$ is a particular solution and the columns of $\boldsymbol{\mathscr{L}}$ are a basis of the null space of $\mathbf{P}^{\mathrm{T}}$. Then, if these constraints are discarded and $\delta\hat{\mathbf{n}}$ is replaced by $\boldsymbol{\mathscr{L}}\hat{\mathbf{x}}$, where $\hat{\mathbf{x}}$ are the new decision variables, the constrained Problem

[2] The weighting matrix $\boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1}$ is symmetric and positive definite, thus of rank S.

(2.120) can be converted to the equivalent unconstrained optimization problem

$$\min_{\hat{\mathbf{x}}} \qquad J_u(\hat{\mathbf{x}}) = \hat{\mathbf{x}}^{\mathrm{T}} \mathscr{L}^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} \mathscr{L} \hat{\mathbf{x}} - 2\hat{\mathbf{x}}^{\mathrm{T}} \mathscr{L}^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} \delta\tilde{\mathbf{n}} + \delta\tilde{\mathbf{n}}^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} \delta\tilde{\mathbf{n}}. \tag{2.123}$$

Since Problem (2.123) is unconstrained and the Hessian matrix $\mathbf{H}(J_u)(\hat{\mathbf{x}}) = 2\mathscr{L}^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} \mathscr{L}$ is positive definite for all $\hat{\mathbf{x}}$,[3] the solution $\hat{\mathbf{x}}^*$ of this problem is given by the stationarity condition

$$\mathbf{0}_{S-q} = \nabla J_u(\hat{\mathbf{x}}^*) = 2\mathscr{L}^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} \mathscr{L} \hat{\mathbf{x}}^* - 2\mathscr{L}^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} \delta\tilde{\mathbf{n}}. \tag{2.124}$$

The matrix $\mathscr{L}^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} \mathscr{L}$ is invertible, hence

$$\hat{\mathbf{x}}^* = \left(\mathscr{L}^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} \mathscr{L} \right)^{-1} \mathscr{L}^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} \delta\tilde{\mathbf{n}} \tag{2.125}$$

and the solution $\delta\hat{\mathbf{n}}^*$ of the constrained Problem (2.120), that is, the optimal reconciled data, is

$$\delta\hat{\mathbf{n}}^* = \mathscr{L}\hat{\mathbf{x}}^* = \mathscr{L} \left(\mathscr{L}^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} \mathscr{L} \right)^{-1} \mathscr{L}^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} \delta\tilde{\mathbf{n}}. \tag{2.126}$$

Since $\mathbf{P}^{\mathrm{T}} \mathscr{L} = \mathbf{0}_{q\times(S-q)}$, the original linear equality constraints $\mathbf{P}^{\mathrm{T}} \delta\hat{\mathbf{n}}^* = \mathbf{0}_q$ are satisfied.

Note that $\hat{\mathbf{x}}^*$ and $\delta\hat{\mathbf{n}}^*$ result from a linear transformation of $\delta\tilde{\mathbf{n}}$ that takes into account the weighting matrix $\boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1}$. Moreover, if there exists some $\tilde{\mathbf{x}}$ such that the measured data $\delta\tilde{\mathbf{n}} = \mathscr{L}\tilde{\mathbf{x}}$, then $\hat{\mathbf{x}}^* = \tilde{\mathbf{x}}$ and $\delta\hat{\mathbf{n}}^* = \mathscr{L}\tilde{\mathbf{x}} = \delta\tilde{\mathbf{n}}$.

2.6 Extensions to Other Lumped Reaction Systems

This section extends the transformation from numbers of moles to extents, shown for homogeneous reaction systems described by numbers of moles and without heat balance, to other lumped reaction systems, namely: homogeneous reaction systems described by concentrations; reaction systems with instantaneous equilibria; multiphase reaction systems; and several lumped reaction systems described by combined material and heat balances. The goal is to show the applicability of this transformation to a wide range of lumped reaction systems.

[3] This can be shown as follows. The matrix $\boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1}$ is symmetric and positive definite, which implies that $\boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1} = \left(\boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1/2}\right)^{\mathrm{T}} \boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1/2}$. Since $\boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1/2}$ is of rank S and $\mathscr{L}$ is of rank $S-q$, the rank of $\boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1/2}\mathscr{L}$ is $S-q$. Then, $\mathscr{L}^{\mathrm{T}}\boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1}\mathscr{L} = \mathscr{L}^{\mathrm{T}}\left(\boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1/2}\right)^{\mathrm{T}}\boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1/2}\mathscr{L} = \left(\boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1/2}\mathscr{L}\right)^{\mathrm{T}}\boldsymbol{\Sigma}_{\delta\tilde{\mathbf{n}}}^{-1/2}\mathscr{L}$ is also of rank $S-q$, thus positive definite and invertible.

2.6.1 Homogeneous reaction systems described by concentrations

2.6.1.1 Volumetric extents $\mathbf{w}_r(t)$, $\mathbf{w}_{in}(t)$ and $w_{ic}(t)$

The volumetric extent of reaction $w_{r,i}(t)$ represents the amount of material that has been processed by the ith reaction and is in the volume at time t. These volumetric extents are described by the ODE

$$\dot{\mathbf{w}}_r(t) = \mathbf{r}(t) - \left(\omega(t) + \frac{\dot{V}(t)}{V(t)}\right)\mathbf{w}_r(t), \qquad \mathbf{w}_r(0) = \mathbf{0}_R. \tag{2.127}$$

The volumetric extent of inlet $w_{in,j}(t)$ represents the amount of material that has flowed into the reactor via the jth inlet and is in the volume at time t. These volumetric extents are described by the ODE

$$\dot{\mathbf{w}}_{in}(t) = \frac{\mathbf{u}_{in}(t)}{V(t)} - \left(\omega(t) + \frac{\dot{V}(t)}{V(t)}\right)\mathbf{w}_{in}(t), \qquad \mathbf{w}_{in}(0) = \mathbf{0}_p. \tag{2.128}$$

The volumetric extent of initial conditions $w_{ic}(t)$ represents the amount of material that was initially in the reactor and is in the volume at time t. This volumetric extent is described by the ODE

$$\dot{w}_{ic}(t) = -\left(\omega(t) + \frac{\dot{V}(t)}{V(t)}\right)w_{ic}(t), \qquad w_{ic}(0) = \frac{1}{V_0}. \tag{2.129}$$

Let us assume that the inlet composition given by $\mathbf{W}_{in}(t)$ is constant. Eq. (2.22) can be reconstructed from Eqs. (2.127), (2.128) and (2.129) using

$$\mathbf{c}(t) = \mathscr{L}\begin{bmatrix}\mathbf{w}_r(t)\\ \mathbf{w}_{in}(t)\\ w_{ic}(t)\end{bmatrix}, \tag{2.130}$$

with $\mathscr{L} = \begin{bmatrix}\mathbf{N}^{\mathrm{T}} & \mathbf{W}_{in} & \mathbf{n}_0\end{bmatrix}$.

Note that the volumetric extents $\mathbf{w}_r(t)$, $\mathbf{w}_{in}(t)$ and $w_{ic}(t)$ are dependent since one volumetric extent is determined by the remaining $R+p$ volumetric extents, which means that only $R+p$ volumetric extents are needed as states and only $R+p$ of the ODEs (2.127), (2.128) and (2.129) are necessary. This can be shown by noticing that the volumetric extents are subject to the constraint

$$\rho(t) = \frac{m(t)}{V(t)} = \frac{\mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{n}(t)}{V(t)} = \mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{c}(t) = \mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathscr{L}\begin{bmatrix}\mathbf{w}_r(t)\\ \mathbf{w}_{in}(t)\\ w_{ic}(t)\end{bmatrix}, \tag{2.131}$$

with $\rho(t)$ a function of the volumetric extents and temperature. However, one additional state is needed to express the dimension of the system, for example $m(t)$, thus the number of states needed to fully describe the system is $R+p+1$.

2.6.1.2 Transformation to volumetric extents

If $\text{rank}(\mathscr{L}) = R+p+1$, the volumetric extents are given by the linear transformation

$$\begin{bmatrix} \mathbf{w}_r(t) \\ \mathbf{w}_{in}(t) \\ w_{ic}(t) \end{bmatrix} = \mathscr{T}\mathbf{c}(t), \tag{2.132}$$

with $\mathscr{T} := \left(\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}\right)^{-1}\mathscr{L}^{\mathrm{T}}\mathbf{W}$.

2.6.1.3 Transformation to invariants

The null space of $\mathscr{L}^{\mathrm{T}}$ is of dimension $q := S - \text{rank}(\mathscr{L})$ and is described by the $S \times q$ matrix $\mathbf{P}$. Then, the q invariants $\mathbf{w}_{iv}(t) = \mathbf{0}_q$ are given by the linear transformation

$$\mathbf{w}_{iv}(t) = \mathbf{P}^{\mathrm{T}}\mathbf{c}(t). \tag{2.133}$$

2.6.2 Reaction systems with instantaneous equilibria

2.6.2.1 Vessel extents $\mathbf{x}_{r,s}(t)$, $\mathbf{x}_{in}(t)$ and $x_{ic}(t)$

The vessel extent of slow reaction $x_{r,s,i}(t)$ represents the amount of material that has been processed by the ith slow reaction and is in the vessel at time t, that is, discounting for the amount that has left the vessel via the outlet. These vessel extents are described by the ODE

$$\dot{\mathbf{x}}_{r,s}(t) = \mathbf{r}_{v,s}(t) - \omega(t)\mathbf{x}_{r,s}(t), \qquad \mathbf{x}_{r,s}(0) = \mathbf{0}_{R_s}. \tag{2.134}$$

The vessel extents of inlet $\mathbf{x}_{in}(t)$ and the vessel extent of initial conditions $x_{ic}(t)$ are described by Eqs. (2.99) and (2.103).

Let us assume that the inlet composition given by $\mathbf{W}_{in}(t)$ is constant. Eq. (2.56) can be reconstructed from Eqs. (2.99), (2.103) and (2.134) using

$$\mathbf{n}_s(t) = \mathscr{L}_s \begin{bmatrix} \mathbf{x}_{r,s}(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \end{bmatrix}, \tag{2.135}$$

with $\mathscr{L}_s = \mathbf{P}_e^{\mathrm{T}}\begin{bmatrix}\mathbf{N}_s^{\mathrm{T}} & \mathbf{W}_{in} & \mathbf{n}_0\end{bmatrix}$.

2.6.2.2 Transformation to vessel extents

If rank $\left(\mathscr{L}_s\right) = R_s + p + 1$, the vessel extents are given by the linear transformation

$$\begin{bmatrix} \mathbf{x}_{r,s}(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \end{bmatrix} = \mathscr{T}_s \mathbf{n}_s(t), \tag{2.136}$$

with $\mathscr{T}_s := \left(\mathscr{L}_s^{\mathrm{T}} \mathbf{W} \mathscr{L}_s\right)^{-1} \mathscr{L}_s^{\mathrm{T}} \mathbf{W}$.

2.6.2.3 Transformation to invariants

The null space of $\mathscr{L}_s^{\mathrm{T}}$ is of dimension $q_s := S_s - \text{rank}\left(\mathscr{L}_s\right)$ and is described by the $S_s \times q_s$ matrix $\mathbf{P}_s$. Then, the q_s invariants $\mathbf{x}_{iv,s}(t) = \mathbf{0}_{q_s}$ are given by the linear transformation

$$\mathbf{x}_{iv,s}(t) = \mathbf{P}_s^{\mathrm{T}} \mathbf{n}_s(t). \tag{2.137}$$

2.6.3 Multiphase reaction systems

2.6.3.1 Vessel extents $\mathbf{x}_{r,f}(t)$, $\mathbf{x}_{m,f}(t)$, $\mathbf{x}_{in,f}(t)$ and $x_{ic,f}(t)$

The vessel extent of reaction $x_{r,f,i}(t)$ represents the amount of material that has been processed by the ith reaction in phase F and is in the vessel at time t, that is, discounting for the amount that has left the vessel via the outlet. These vessel extents are described by the ODE

$$\dot{\mathbf{x}}_{r,f}(t) = \mathbf{r}_{v,f}(t) - \omega_f(t)\mathbf{x}_{r,f}(t), \qquad \mathbf{x}_{r,f}(0) = \mathbf{0}_{R_f}. \tag{2.138}$$

The vessel extent of mass transfer $x_{m,f,k}(t)$ represents the amount of material that has transferred to phase F via the kth mass transfer and is in the vessel at time t, that is, discounting for the amount that has left the vessel via the outlet. These vessel extents are described by the ODE

$$\dot{\mathbf{x}}_{m,f}(t) = \boldsymbol{\phi}_{m,f}^{v}(t) - \omega_f(t)\mathbf{x}_{m,f}(t), \qquad \mathbf{x}_{m,f}(0) = \mathbf{0}_{p_{m,f}}. \tag{2.139}$$

The vessel extent of inlet $x_{in,f,j}(t)$ represents the amount of material that has flowed into phase F in the reactor via the jth inlet and is in the vessel at time t, that is, discounting for the amount that has left the vessel via the outlet. These vessel extents are described by the ODE

$$\dot{\mathbf{x}}_{in,f}(t) = \mathbf{u}_{in,f}(t) - \omega_f(t)\mathbf{x}_{in,f}(t), \qquad \mathbf{x}_{in,f}(0) = \mathbf{0}_{p_f}. \tag{2.140}$$

The vessel extent of initial conditions $x_{ic,f}(t)$ represents the amount of material that

was initially in phase F in the reactor and is in the vessel at time t, that is, discounting for the amount that has left the vessel via the outlet. This vessel extent is described by the ODE

$$\dot{x}_{ic,f}(t) = -\omega_f(t) x_{ic,f}(t), \qquad x_{ic,f}(0) = 1. \tag{2.141}$$

Let us assume that the inlet composition given by $\mathbf{W}_{in,f}(t)$ is constant. Eq. (2.63) can be reconstructed from Eqs. (2.138), (2.139), (2.140) and (2.141) using

$$\mathbf{n}_f(t) = \mathscr{L}_f \begin{bmatrix} \mathbf{x}_{r,f}(t) \\ \mathbf{x}_{m,f}(t) \\ \mathbf{x}_{in,f}(t) \\ x_{ic,f}(t) \end{bmatrix}, \tag{2.142}$$

with $\mathscr{L}_f = \begin{bmatrix} \mathbf{N}_f^{\mathrm{T}} & \mathbf{E}_{m,f} & \mathbf{W}_{in,f} & \mathbf{n}_{f,0} \end{bmatrix}$.

2.6.3.2 Transformation to vessel extents

If $\operatorname{rank}\left(\mathscr{L}_f\right) = R_f + p_{m,f} + p_f + 1$, the vessel extents are given by the linear transformation

$$\begin{bmatrix} \mathbf{x}_{r,f}(t) \\ \mathbf{x}_{m,f}(t) \\ \mathbf{x}_{in,f}(t) \\ x_{ic,f}(t) \end{bmatrix} = \mathscr{T}_f \mathbf{n}_f(t), \tag{2.143}$$

with $\mathscr{T}_f := \left(\mathscr{L}_f^{\mathrm{T}} \mathbf{W} \mathscr{L}_f\right)^{-1} \mathscr{L}_f^{\mathrm{T}} \mathbf{W}$.

2.6.3.3 Transformation to invariants

The null space of $\mathscr{L}_f^{\mathrm{T}}$ is of dimension $q_f := S_f - \operatorname{rank}\left(\mathscr{L}_f\right)$ and is described by the $S_f \times q_f$ matrix $\mathbf{P}_f$. Then, the q_f invariants $\mathbf{x}_{iv,f}(t) = \mathbf{0}_{q_f}$ are given by the linear transformation

$$\mathbf{x}_{iv,f}(t) = \mathbf{P}_f^{\mathrm{T}} \mathbf{n}_f(t). \tag{2.144}$$

2.6.4 Combined material and heat balance equations

The combined material and heat balance equations for homogeneous reaction systems, reaction systems with instantaneous equilibria, and multiphase reaction systems are described in Appendix A.4.

3 Concept of Extents for Distributed Reaction Systems

This chapter is adapted from the postprint of the following article [81]:

D. Rodrigues, J. Billeter, and D. Bonvin. Generalization of the concept of extents to distributed reaction systems. *Chem. Eng. Sci.*, 171:558–575, 2017.

Link: http://doi.org/10.1016/j.ces.2017.05.051.

The author of this thesis contributed to that article by developing the main novel ideas, implementing the simulations, and writing a significant part of the text. Hence, the author retains the right to include the article in this thesis since it is not published commercially and the journal is referenced as the original source.

3.1 Introduction

The chemical industry uses chemical reactions and physical transformations to convert raw materials and energy into products. To operate these industrial chemical processes in a reliable and efficient manner, process models are typically used for design, monitoring, estimation, control and optimization. If each phase can be assumed to be well mixed, a dynamic model describes the time evolution of the system via ordinary differential equations (ODEs). The model consists of material and energy balances and includes information about the reactions (stoichiometry, kinetics, enthalpies of reaction), the transfer of mass and energy within and between phases, and the operating conditions (inlet and outlet flows, initial conditions and exchanges with the environment). Details about chemical reactor modeling and analysis can be found in many textbooks, for example [82, 83, 84].

The modeling of the rate processes at work is often challenging. The difficulty arises from the coupling between the different chemical and physical effects, as in the case of two-phase reaction systems, where the different reactions are inherently coupled with each other and with the mass-transfer phenomena. For lumped reaction systems, the concept of *vessel extents* is very useful, as the transformation of the original states (concentrations and temperatures) to these extents allows isolating the contributions of the reactions, mass

transfers and inlet flows [18, 19], as shown in Chapter 2.

In this chapter, the assumption of perfect mixing within each phase is relaxed. Inhomogeneity can result from either a technical flaw, as in reactors with poor mixing, or a technical choice, as in tubular reactors [85], micro-reactors [86], reactive distillation columns [87] or reactive absorption columns [88]. These distributed reaction systems (resolved in time and space) are typically described by partial differential equations (PDEs) that couple the effects of reaction, mass transfer, diffusion, and initial and boundary conditions. The coupling of distributed reaction systems in time and space complicates their analysis. These systems are also complex to analyze due to the existence of boundary conditions, which are not present in lumped reaction systems.

The concept of extents, and of variant and invariant states in general, which aims at decoupling the various rate processes at play and thereby simplifying their analysis, has hardly been applied to distributed reaction systems. Yet, an early work describes the use of variant and invariant states for the simulation of a plug-flow reactor, resulting in reduced computational time [29]. Furthermore, a transformation to reaction-invariant compositions in reactive distillation columns was proposed to reduce the number of degrees of freedom in process design [49]. This transformation to reaction invariants was later applied to reactive chromatography and membrane reactors [50].

This chapter considers the modeling of distributed reaction systems from a methodological standpoint. The concept of extents and the transformation of the original states (concentrations and temperature) to these extents are discussed. Emphasis is given to the conceptual understanding of extents. The introduction of the concept of extents for distributed reaction systems is expected to help design and operate this class of processes.

The chapter is organized as follows. Section 3.2 presents the extension of the concept of extents from a lumped reaction system described by ODEs to a simple plug-flow reactor described by PDEs. Section 3.3 describes tubular reactors in terms of extents for different situations (single-phase, multiphase, one-dimensional, two-dimensional). Section 3.4 introduces the concept of extents for reactive separation columns, such as packed and tray columns. Section 3.5 presents the concept of extents for a generic multiphase distributed reaction system. Section 3.6 discusses four case studies illustrating the use of extents, while Section 3.7 concludes the chapter.

3.2 From Lumped to Distributed Reaction Systems

3.2.1 Single-phase lumped reactors

In single-phase lumped reactors, the concentrations and temperature are functions of the time t only, the spatial coordinates being eliminated under the assumption that the phase is isotropic (well mixed).

3.2.1.1 Material balance equations, $\mathbf{n}(t)$

Let us consider a lumped reactor. The S-dimensional vector of numbers of moles $\mathbf{n}(t)$ is described by the ODE

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{n}(t) + \omega(t)\,\mathbf{n}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}(t)\mathbf{u}_{in}(t), \quad \mathbf{n}(0) = \mathbf{n}_0, \tag{3.1}$$

where $\mathbf{r}_v(t) := V(t)\mathbf{r}(t)$, with $\mathbf{r}(t)$ the R-dimensional vector of reaction rates and $V(t)$ the volume, $\mathbf{N}$ is the $R \times S$ stoichiometric matrix, $\mathbf{u}_{in}(t)$ is the p-dimensional vector of inlet mass flowrates, $\mathbf{W}_{in}(t)$ is the $S \times p$ inlet composition matrix, whose jth column is $\mathbf{W}_{in,j}(t) := \mathbf{M}_w^{-1}\check{\mathbf{w}}_{in,j}(t)$, with $\mathbf{M}_w$ the S-dimensional diagonal matrix of molecular weights and $\check{\mathbf{w}}_{in,j}(t)$ the S-dimensional vector of weight fractions of the jth inlet, and $\omega(t) := \frac{u_{out}(t)}{m(t)}$ is the inverse of the residence time, with $u_{out}(t)$ the outlet mass flowrate and $m(t)$ the mass. The concentrations $\mathbf{c}(t)$ can be computed as $\frac{\mathbf{n}(t)}{V(t)}$. The initial conditions $\mathbf{n}_0$ are denoted IC and the inlet flow conditions related to $\mathbf{W}_{in}$ and $\mathbf{u}_{in}$ are denoted IFC.

Remark 3.1. Throughout the chapter, the rates associated with each rate process are modeled as signals that vary in time (and space), which hides the fact that the rates depend on concentrations and temperature that vary in time (and space). For example, in this lumped reactor, the reaction rates are written as $\mathbf{r}(t)$, but in fact they depend on $\mathbf{c}(t)$ and $T(t)$. For the sake of conciseness, the time dependence of the various variables is omitted as much as possible in the remainder.

3.2.1.2 Effect of the outlet on the IC and IFC

The effect of the outlet flow on the initial and inlet flow conditions can be computed as $\mathbf{n}_{iic}(t)$ by solving the ODE

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{n}_{iic} + \omega\,\mathbf{n}_{iic} = \mathbf{W}_{in}\mathbf{u}_{in}, \quad \mathbf{n}_{iic}(0) = \mathbf{n}_0. \tag{3.2}$$

3.2.1.3 Vessel extents of reaction $\mathbf{x}_r(t)$

The vessel extent of reaction $x_{r,i}(t)$ represents the amount of material that has been processed by the ith reaction and is in the vessel at time t, that is, discounting for the amount that has left the vessel via the outlet. These vessel extents are described by the ODE

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{x}_r + \omega\,\mathbf{x}_r = \mathbf{r}_v, \quad \mathbf{x}_r(0) = \mathbf{0}_R. \tag{3.3}$$

Eq. (3.1) can be reconstructed from Eqs. (3.2) and (3.3) using

$$\mathbf{n} = \mathscr{L}\,\mathbf{x}_r + \mathbf{n}_{iic}, \tag{3.4}$$

with $\mathscr{L} = \mathbf{N}^{\mathrm{T}}$.

3.2.1.4 Transformation to vessel extents

The vessel extents $\mathbf{x}_r$ can be computed from the numbers of moles $\mathbf{n}$ by inversion of Eq. (3.4). If $\text{rank}(\mathscr{L}) = R$, then $\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}$ is invertible for any positive definite weighting matrix $\mathbf{W}$ of dimension S, and the vessel extents of reaction are given by the linear transformation

$$\mathbf{x}_r = \mathscr{T}\,\delta\mathbf{n}, \tag{3.5}$$

with $\mathscr{T} := \left(\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}\right)^{-1}\mathscr{L}^{\mathrm{T}}\mathbf{W}$, and $\delta\mathbf{n} := \mathbf{n} - \mathbf{n}_{iic}$. Note that, for $\mathbf{W} = \mathbf{I}_S$, $\mathscr{T}$ is the Moore-Penrose pseudoinverse of $\mathscr{L}$.

Remark 3.2. The vessel extents $\mathbf{x}_r(t)$ described by ODE (3.3) and computed from $\mathbf{n}(t)$ via Eq. (3.5) represent the R reaction variants in the system. As shown in Section 2.5, one can describe and compute from $\mathbf{n}(t)$ additional vessel extents (of inlet flows and initial conditions) as well as invariant quantities.

3.2.1.5 Combined material and heat balance equations

The combined material and heat balance equations are described in Appendix B.1.1.

3.2.2 Single-phase plug-flow reactors

In single-phase plug-flow reactors, the concentrations and temperature are functions of the spatial coordinate z and the time t. It is assumed that the inlet of the reaction system is located at $z = 0$ and z is positive along the reactor length.

3.2.2.1 Material balance equations, $\mathbf{c}(z,t)$

Let us assume a distributed reaction system in the spatial dimension z without diffusion (advection–reaction problem). The S-dimensional vector of concentrations $\mathbf{c}(z,t)$ is described by the PDE

$$\frac{\partial}{\partial t}\mathbf{c}(z,t) + \frac{\partial}{\partial z}\big(v_z(z,t)\mathbf{c}(z,t)\big) = \mathbf{N}^{\mathrm{T}}\mathbf{r}(z,t), \tag{3.6}$$

where $v_z(z,t)$ is the advective velocity in the z-direction.

Eq. (3.6) is subject to the following initial conditions (IC) and advective boundary conditions (BC):

$$\mathbf{c}(z,0) = \mathbf{c}_0(z), \quad \forall z > 0 \quad \text{(IC)},$$
$$\mathbf{c}(0,t) = \mathbf{c}_{in}(t), \quad \forall t \geq 0 \quad \text{(BC)}.$$

Remark 3.3. For the sake of conciseness, the spatial and time dependences of the various

variables are omitted as much as possible in the remainder.

3.2.2.2 Effect of advection on the IC and BC

The effect of advection on the initial and advective boundary conditions can be computed as $\mathbf{c}_{ibc}(z,t)$ by solving the PDE

$$\frac{\partial}{\partial t}\mathbf{c}_{ibc} + \frac{\partial}{\partial z}\left(v_z \mathbf{c}_{ibc}\right) = \mathbf{0}_S, \tag{3.7}$$

with the initial and boundary conditions

$$\mathbf{c}_{ibc}(z,0) = \mathbf{c}_0(z), \quad \forall z > 0 \quad \text{(IC)}, \tag{3.8}$$
$$\mathbf{c}_{ibc}(0,t) = \mathbf{c}_{in}(t), \quad \forall t \geq 0 \quad \text{(BC)}. \tag{3.9}$$

3.2.2.3 Extents of reaction $\mathbf{x}_r(z,t)$

The extent of reaction $x_{r,i}(z,t)$ represents the amount of material that has been processed by the ith reaction and is at position z at time t. These extents are described by the PDE

$$\frac{\partial}{\partial t}\mathbf{x}_r + \frac{\partial}{\partial z}\left(v_z \mathbf{x}_r\right) = \mathbf{r}, \tag{3.10}$$

with $\mathbf{x}_r(z,0) = \mathbf{0}_R, \forall z > 0$ (IC), and $\mathbf{x}_r(0,t) = \mathbf{0}_R, \forall t \geq 0$ (BC).

Eq. (3.6) can be reconstructed from Eqs. (3.7) and (3.10) using

$$\mathbf{c} = \mathscr{L}\,\mathbf{x}_r + \mathbf{c}_{ibc}, \tag{3.11}$$

with $\mathscr{L} = \mathbf{N}^{\mathrm{T}}$.

3.2.2.4 Transformation to extents

The extents $\mathbf{x}_r$ can be computed from the concentrations $\mathbf{c}$ by inversion of Eq. (3.11). If $\mathrm{rank}(\mathscr{L}) = R$, the extents of reaction are given by the linear transformation

$$\mathbf{x}_r = \mathscr{T}\,\delta\mathbf{c}, \tag{3.12}$$

with $\mathscr{T} := \left(\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}\right)^{-1}\mathscr{L}^{\mathrm{T}}\mathbf{W}$, and $\delta\mathbf{c} := \mathbf{c} - \mathbf{c}_{ibc}$.

3.2.2.5 Combined material and heat balance equations

The combined material and heat balance equations are described in Appendix B.1.2.

3.3 Tubular Reactors

This section presents dynamic models for tubular reactors, building up from the simple plug-flow model presented in the previous section by progressively increasing the complexity of the model.

3.3.1 Single-phase one-dimensional tubular reactors

Since the concentrations vary with the spatial coordinate, the concentration gradients might lead to significant diffusion if the flow of material is not dominated by advection. Hence, the model of a single-phase one-dimensional tubular reactor considers diffusion rates (advection–axial diffusion–reaction problem).

3.3.1.1 Material balance equations, $\mathbf{c}(z,t)$

The concentrations $\mathbf{c}(z,t)$ are described by the PDE

$$\frac{\partial}{\partial t}\mathbf{c} + \frac{\partial}{\partial z}\left(v_z\mathbf{c}\right) = \mathbf{N}^{\mathrm{T}}\mathbf{r} + \mathbf{E}_d\boldsymbol{\phi}_d, \tag{3.13}$$

where $\boldsymbol{\phi}_d$ is the p_d-dimensional vector of diffusion rates, $\mathbf{E}_d$ is an $S \times p_d$ matrix with each row having one element equal to 1 if the corresponding species diffuses and the remaining elements equal to 0, and p_d is the number of diffusing species. Note that the diffusion rates might differ significantly for the various species, thus leading to the simplifying assumption that some of the species do not diffuse at all.

Diffusion calls for the definition of a p_d-dimensional vector of diffusion fluxes in the z-direction, denoted $\mathbf{j}_{d,z}(z,t)$, which is described by the PDE

$$\frac{\partial}{\partial z}\mathbf{j}_{d,z} = -\boldsymbol{\phi}_d, \tag{3.14}$$

with the diffusive boundary conditions[1]

$$\lim_{z\to\infty}\mathbf{j}_{d,z}(z,t) = \mathbf{0}_{p_d},\ \forall t \geq 0.$$

Eq. (3.13) is subject to the following initial and advective boundary conditions:

$$\begin{aligned}
&\mathbf{c}(z,0) = \mathbf{c}_0(z), && \forall z > 0 \quad \text{(IC)},\\
&\mathbf{c}(0,t) = \mathbf{c}_{in}(t) + \mathbf{c}_d(t), && \forall t \geq 0 \quad \text{(BC)},
\end{aligned}$$

with $\mathbf{c}_d(t) := -\frac{\mathbf{E}_d\,\mathbf{j}_{d,z}(0,t)}{\beta v_z(0,t)}$. These initial and boundary conditions are also affected by those

[1] These boundary conditions correspond to what is called "approximation by a reactor of infinite length", since the boundary conditions are given at $z = 0$ and $z \to \infty$ [89]. Note that the approach also applies when different boundary conditions are assumed.

of Eq. (3.14). Note that $\beta \to \infty$ if the boundary conditions are of the first type (Dirichlet boundary conditions), whereas $\beta = 1$ if the boundary conditions are of the third type (Robin boundary conditions) [90].

3.3.1.2 Effect of advection on the IC and BC

The effect of advection on the initial and advective boundary conditions can be computed by solving Eq. (3.7), with the initial and boundary conditions given by Eqs. (3.8) and (3.9).

3.3.1.3 Extents $\mathbf{x}_r(z,t)$ and $\mathbf{x}_d(z,t)$

The extents of reaction $\mathbf{x}_r(z,t)$ are described by Eq. (3.10), with the corresponding initial and boundary conditions.

The extent of diffusion $x_{d,j}(z,t)$ represents the amount of material that has transferred via the jth diffusion rate and is at position z at time t. These extents are described by the PDE

$$\frac{\partial}{\partial t}\mathbf{x}_d + \frac{\partial}{\partial z}\left(v_z \mathbf{x}_d\right) = \boldsymbol{\phi}_d, \tag{3.15}$$

with $\mathbf{x}_d(z,0) = \mathbf{0}_{p_d}, \forall z > 0$ (IC), and $\mathbf{x}_d(0,t) = -\frac{\mathbf{j}_{d,z}(0,t)}{\beta v_z(0,t)}, \forall t \geq 0$ (BC).

Eq. (3.13) can be reconstructed from Eqs. (3.7), (3.10) and (3.15) using

$$\mathbf{c} = \mathscr{L}\begin{bmatrix}\mathbf{x}_r \\ \mathbf{x}_d\end{bmatrix} + \mathbf{c}_{ibc}, \tag{3.16}$$

with $\mathscr{L} = \begin{bmatrix}\mathbf{N}^{\mathrm{T}} & \mathbf{E}_d\end{bmatrix}$.

3.3.1.4 Transformation to extents

If $\operatorname{rank}(\mathscr{L}) = R + p_d$, the extents of reaction and diffusion are given by the linear transformation

$$\begin{bmatrix}\mathbf{x}_r \\ \mathbf{x}_d\end{bmatrix} = \mathscr{T}\,\delta\mathbf{c}, \tag{3.17}$$

with $\mathscr{T} := \left(\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}\right)^{-1}\mathscr{L}^{\mathrm{T}}\mathbf{W}$, and $\delta\mathbf{c} := \mathbf{c} - \mathbf{c}_{ibc}$.

Remark 3.4. The rank condition associated with this linear transformation implies that $p_d \leq S - R$.

3.3.1.5 Combined material and heat balance equations

The combined material and heat balance equations are described in Appendix B.1.3.

3.3.2 Multiphase one-dimensional tubular reactors

Let us now consider a one-dimensional tubular reactor with multiple phases. Let us assume that each phase F is well mixed in the direction orthogonal to z and exchanges material with other phases by mean of mass transfers (advection–axial diffusion–mass transfer–reaction problem).

The subscript $(\cdot)_f$ is introduced to denote quantities that are related to phase F. As each phase occupies a certain fraction of the reactor volume, the variable $\varepsilon_f(z,t)$ defines the volumetric fraction occupied by phase F at position z at time t. Then, for any variable $y_f(z,t)$ that represents a certain quantity per unit volume of phase F, $y_f^\varepsilon(z,t) := \varepsilon_f(z,t)\, y_f(z,t)$ defines the corresponding quantity per unit total volume.

3.3.2.1 Material balance equations, $\mathbf{c}_f^\varepsilon(z,t)$

The S_f-dimensional vector of concentrations $\mathbf{c}_f^\varepsilon(z,t)$ is described by the PDE

$$\frac{\partial}{\partial t}\mathbf{c}_f^\varepsilon + \frac{\partial}{\partial z}\left(v_{f,z}\mathbf{c}_f^\varepsilon\right) = \mathbf{N}_f^{\mathrm{T}}\mathbf{r}_f^\varepsilon + \mathbf{E}_{m,f}\,\boldsymbol{\phi}_{m,f}^\varepsilon + \mathbf{E}_{d,f}\,\boldsymbol{\phi}_{d,f}^\varepsilon, \tag{3.18}$$

where $\boldsymbol{\phi}_{m,f}^\varepsilon$ is the $p_{m,f}$-dimensional vector of molar mass-transfer rates per unit total volume describing the material transferred to phase F, $\mathbf{E}_{m,f}$ is an $S_f \times p_{m,f}$ matrix with each row having one element equal to 1 if the corresponding species is transferred to phase F and the remaining elements equal to 0, and $p_{m,f}$ is the number of species transferring to or from phase F. Note that, if a given phase is fixed, its velocity $v_{f,z}$ is zero.

The $p_{d,f}$-dimensional vector of diffusion fluxes in the z-direction, denoted $\mathbf{j}_{d,f,z}^\varepsilon(z,t)$, is described by the PDE

$$\frac{\partial}{\partial z}\mathbf{j}_{d,f,z}^\varepsilon = -\boldsymbol{\phi}_{d,f}^\varepsilon, \tag{3.19}$$

with the diffusive boundary conditions

$$\lim_{z\to\infty}\mathbf{j}_{d,f,z}^\varepsilon(z,t) = \mathbf{0}_{p_{d,f}},\ \forall t \geq 0.$$

Eq. (3.18) is subject to the following initial and advective boundary conditions:

$$\begin{aligned}
&\mathbf{c}_f^\varepsilon(z,0) = \mathbf{c}_{f,0}^\varepsilon(z), && \forall z > 0 \quad \text{(IC)},\\
&\mathbf{c}_f^\varepsilon(0,t) = \mathbf{c}_{f,in}^\varepsilon(t) + \mathbf{c}_{d,f}^\varepsilon(t), && \forall t \geq 0 \quad \text{(BC)},
\end{aligned}$$

with $\mathbf{c}^{\varepsilon}_{d,f}(t) := -\frac{\mathbf{E}_{d,f}\mathbf{j}^{\varepsilon}_{d,f,z}(0,t)}{\beta v_{f,z}(0,t)}$.

3.3.2.2 Effect of advection on the IC and BC

The effect of advection on the initial and advective boundary conditions can be computed as $\mathbf{c}^{\varepsilon}_{ibc,f}(z,t)$ by solving the PDE

$$\frac{\partial}{\partial t}\mathbf{c}^{\varepsilon}_{ibc,f} + \frac{\partial}{\partial z}\left(v_{f,z}\mathbf{c}^{\varepsilon}_{ibc,f}\right) = \mathbf{0}_{S_f}, \tag{3.20}$$

with the initial and boundary conditions

$$\mathbf{c}^{\varepsilon}_{ibc,f}(z,0) = \mathbf{c}^{\varepsilon}_{f,0}(z), \quad \forall z > 0 \quad \text{(IC)}, \tag{3.21}$$

$$\mathbf{c}^{\varepsilon}_{ibc,f}(0,t) = \mathbf{c}^{\varepsilon}_{f,in}(t), \quad \forall t \geq 0 \quad \text{(BC)}. \tag{3.22}$$

3.3.2.3 Extents $\mathbf{x}_{r,f}(z,t)$, $\mathbf{x}_{m,f}(z,t)$ and $\mathbf{x}_{d,f}(z,t)$

The extent of reaction $x_{r,f,i}(z,t)$ represents the amount of material that has been processed by the ith reaction in phase F and is at position z at time t. These extents are described by the PDE

$$\frac{\partial}{\partial t}\mathbf{x}_{r,f} + \frac{\partial}{\partial z}\left(v_{f,z}\mathbf{x}_{r,f}\right) = \mathbf{r}^{\varepsilon}_{f}, \tag{3.23}$$

with $\mathbf{x}_{r,f}(z,0) = \mathbf{0}_{R_f}, \forall z > 0$ (IC), and $\mathbf{x}_{r,f}(0,t) = \mathbf{0}_{R_f}, \forall t \geq 0$ (BC).

The extent of mass transfer $x_{m,f,k}(z,t)$ represents the amount of material that has transferred to phase F via the kth mass transfer and is at position z at time t. These extents are described by the PDE

$$\frac{\partial}{\partial t}\mathbf{x}_{m,f} + \frac{\partial}{\partial z}\left(v_{f,z}\mathbf{x}_{m,f}\right) = \boldsymbol{\phi}^{\varepsilon}_{m,f}, \tag{3.24}$$

with $\mathbf{x}_{m,f}(z,0) = \mathbf{0}_{p_{m,f}}, \forall z > 0$ (IC), and $\mathbf{x}_{m,f}(0,t) = \mathbf{0}_{p_{m,f}}, \forall t \geq 0$ (BC).

The extent of diffusion $x_{d,f,j}(z,t)$ represents the amount of material that has transferred via the jth diffusion rate in phase F and is at position z at time t. These extents are described by the PDE

$$\frac{\partial}{\partial t}\mathbf{x}_{d,f} + \frac{\partial}{\partial z}\left(v_{f,z}\mathbf{x}_{d,f}\right) = \boldsymbol{\phi}^{\varepsilon}_{d,f}, \tag{3.25}$$

with $\mathbf{x}_{d,f}(z,0) = \mathbf{0}_{p_{d,f}}, \forall z > 0$ (IC), and $\mathbf{x}_{d,f}(0,t) = -\frac{\mathbf{j}^{\varepsilon}_{d,f,z}(0,t)}{\beta v_{f,z}(0,t)}, \forall t \geq 0$ (BC).

Eq. (3.18) can be reconstructed from Eqs. (3.20) and (3.23)-(3.25) using

$$\mathbf{c}_f^{\varepsilon} = \mathscr{L}_f \begin{bmatrix} \mathbf{x}_{r,f} \\ \mathbf{x}_{m,f} \\ \mathbf{x}_{d,f} \end{bmatrix} + \mathbf{c}_{ibc,f}^{\varepsilon}, \tag{3.26}$$

with $\mathscr{L}_f = \begin{bmatrix} \mathbf{N}_f^{\mathrm{T}} & \mathbf{E}_{m,f} & \mathbf{E}_{d,f} \end{bmatrix}$.

3.3.2.4 Transformation to extents

If $\operatorname{rank}\left(\mathscr{L}_f\right) = R_f + p_{m,f} + p_{d,f}$, the extents of reaction, mass transfer and diffusion are given by the linear transformation

$$\begin{bmatrix} \mathbf{x}_{r,f} \\ \mathbf{x}_{m,f} \\ \mathbf{x}_{d,f} \end{bmatrix} = \mathscr{T}_f \, \delta \mathbf{c}_f^{\varepsilon}, \tag{3.27}$$

with $\mathscr{T}_f := \left(\mathscr{L}_f^{\mathrm{T}} \mathbf{W} \mathscr{L}_f\right)^{-1} \mathscr{L}_f^{\mathrm{T}} \mathbf{W}$, and $\delta \mathbf{c}_f^{\varepsilon} := \mathbf{c}_f^{\varepsilon} - \mathbf{c}_{ibc,f}^{\varepsilon}$.
Remark 3.5. The rank condition associated with this linear transformation implies that $p_{m,f} \leq S_f - R_f - p_{d,f}$.

3.3.2.5 Combined material and heat balance equations

The combined material and heat balance equations are described in Appendix B.1.4.

3.3.3 Multiphase two-dimensional tubular reactors

Let us relax the assumptions of perfect radial mixing at each position z and consider a tubular reactor of radius $\mathscr{R}$ where all the quantities depend on the axial coordinate z and the radial distance r. Then, all the variables that were functions of z and t now become functions of z, r and t. Furthermore, the concentration gradients in the r-direction generate diffusion fluxes in that direction (advection–axial and radial diffusion–mass transfer–reaction problem).

3.3.3.1 Material balance equations, $\mathbf{c}_f^{\varepsilon}(z,r,t)$

The concentrations $\mathbf{c}_f^{\varepsilon}(z,r,t)$ are described by the PDE in Eq. (3.18).

The $p_{d,f}$-dimensional vectors of diffusion fluxes in the radial direction r and axial direction z, denoted $\mathbf{j}_{d,f,r}^{\varepsilon}(z,r,t)$ and $\mathbf{j}_{d,f,z}^{\varepsilon}(z,r,t)$, are described by the PDE

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\,\mathbf{j}_{d,f,r}^{\varepsilon}\right) + \frac{\partial}{\partial z}\mathbf{j}_{d,f,z}^{\varepsilon} = -\boldsymbol{\phi}_{d,f}^{\varepsilon}, \tag{3.28}$$

with the diffusive boundary conditions

$$\begin{aligned}
\mathbf{j}^{\varepsilon}_{d,f,r}(z,0,t) &= \mathbf{0}_{p_{d,f}}, \quad \forall z \geq 0, \quad \forall t \geq 0,\\
\mathbf{j}^{\varepsilon}_{d,f,r}(z,\mathscr{R},t) &= \mathbf{0}_{p_{d,f}}, \quad \forall z \geq 0, \quad \forall t \geq 0,\\
\lim_{z\to\infty} \mathbf{j}^{\varepsilon}_{d,f,z}(z,r,t) &= \mathbf{0}_{p_{d,f}}, \ \forall r \in]0,\mathscr{R}[, \forall t \geq 0.
\end{aligned}$$

Eq. (3.18) is subject to the following initial and advective boundary conditions:

$$\begin{aligned}
&\mathbf{c}^{\varepsilon}_{f}(z,r,0) = \mathbf{c}^{\varepsilon}_{f,0}(z,r), \qquad \forall z > 0, \ \forall r \in]0,\mathscr{R}[\ \text{(IC)},\\
&\mathbf{c}^{\varepsilon}_{f}(0,r,t) = \mathbf{c}^{\varepsilon}_{f,in}(r,t) + \mathbf{c}^{\varepsilon}_{d,f}(r,t), \ \forall r \in]0,\mathscr{R}[, \ \forall t \geq 0 \ \text{(BC)},
\end{aligned}$$

with $\mathbf{c}^{\varepsilon}_{d,f}(r,t) := -\frac{\mathbf{E}_{d,f}\mathbf{j}^{\varepsilon}_{d,f,z}(0,r,t)}{\beta \nu_{f,z}(0,r,t)}$.

3.3.3.2 Effect of advection on the IC and BC

The effect of advection on the initial and advective boundary conditions can be computed as $\mathbf{c}^{\varepsilon}_{ibc,f}(z,r,t)$ by solving Eq. (3.20), with the initial and boundary conditions

$$\begin{aligned}
&\mathbf{c}^{\varepsilon}_{ibc,f}(z,r,0) = \mathbf{c}^{\varepsilon}_{f,0}(z,r), \quad \forall z > 0, \ \forall r \in]0,\mathscr{R}[\quad \text{(IC)},\\
&\mathbf{c}^{\varepsilon}_{ibc,f}(0,r,t) = \mathbf{c}^{\varepsilon}_{f,in}(r,t), \quad \forall r \in]0,\mathscr{R}[, \ \forall t \geq 0 \quad \text{(BC)}.
\end{aligned}$$

3.3.3.3 Extents $\mathbf{x}_{r,f}(z,r,t)$, $\mathbf{x}_{m,f}(z,r,t)$ and $\mathbf{x}_{d,f}(z,r,t)$

The extents of reaction $\mathbf{x}_{r,f}(z,r,t)$ are computed via Eq. (3.23), with $\mathbf{x}_{r,f}(z,r,0) = \mathbf{0}_{R_f}$, $\forall z > 0$, $\forall r \in]0,\mathscr{R}[$ (IC) and $\mathbf{x}_{r,f}(0,r,t) = \mathbf{0}_{R_f}$, $\forall r \in]0,\mathscr{R}[$, $\forall t \geq 0$ (BC).

The extents of mass transfer $\mathbf{x}_{m,f}(z,r,t)$ are computed via Eq. (3.24), with $\mathbf{x}_{m,f}(z,r,0) = \mathbf{0}_{p_{m,f}}$, $\forall z > 0$, $\forall r \in]0,\mathscr{R}[$ (IC) and $\mathbf{x}_{m,f}(0,r,t) = \mathbf{0}_{p_{m,f}}$, $\forall r \in]0,\mathscr{R}[$, $\forall t \geq 0$ (BC).

The extents of diffusion $\mathbf{x}_{d,f}(z,r,t)$ are computed via Eq. (3.25), with $\mathbf{x}_{d,f}(z,r,0) = \mathbf{0}_{p_{d,f}}$, $\forall z > 0$, $\forall r \in]0,\mathscr{R}[$ (IC) and $\mathbf{x}_{d,f}(0,r,t) = -\frac{\mathbf{j}^{\varepsilon}_{d,f,z}(0,r,t)}{\beta \nu_{f,z}(0,r,t)}$, $\forall r \in]0,\mathscr{R}[$, $\forall t \geq 0$ (BC).

Eq. (3.18) for $\mathbf{c}^{\varepsilon}_{f}(z,r,t)$ can be reconstructed from Eqs. (3.20) and (3.23)-(3.25) using Eq. (3.26).

3.3.3.4 Transformation to extents

If $\operatorname{rank}\left(\mathscr{L}_f\right) = R_f + p_{m,f} + p_{d,f}$, the extents of reaction, mass transfer and diffusion are given by the linear transformation in Eq. (3.27).

3.3.3.5 Combined material and heat balance equations

The combined material and heat balance equations are described in Appendix B.1.5.

3.4 Reactive Separation Columns

This section deals with reactive separation columns, such as those used in reactive distillation and reactive absorption. Two models are discussed, for packed and tray columns. The main difference is that packed columns are typically modeled as distributed systems described by PDEs, whereas tray columns can be modeled as staged processes described by ODEs.

Unlike tubular reactors, reactive separation columns can have intermediate inlet and outlet streams. A common simplification in the modeling of reactive separation columns consists in considering only balances in the liquid phase L and neglecting the diffusion and heat conduction rates[2]. For the sake of notation, it is assumed that the liquid inlet is located at $z = 0$ and z is positive inside the column.

3.4.1 Packed reactive separation columns

If a reactive separation column of constant cross-section area A is modeled as a continuous column with perfect radial mixing and no diffusion, the model is that of a plug-flow reactor with additional mass transfer (advection–mass transfer–reaction problem).

3.4.1.1 Material balance equations, $\mathbf{c}_l^{\varepsilon}(z,t)$

The S_l-dimensional vector of concentrations $\mathbf{c}_l^{\varepsilon}(z,t)$ is described by the PDE

$$\frac{\partial}{\partial t}\mathbf{c}_l^{\varepsilon} + \frac{\partial}{\partial z}\left(v_{l,z}\mathbf{c}_l^{\varepsilon}\right) = \mathbf{N}_l^{\mathrm{T}}\mathbf{r}_l^{\varepsilon} + \mathbf{E}_{m,l}\boldsymbol{\phi}_{m,l}^{\varepsilon}, \tag{3.29}$$

where $v_{l,z}(z,t) := \frac{L(z,t)}{n_{h,l}(z,t)}$ is the advective velocity, with $L(z,t)$ the molar advective flowrate of the liquid phase and $n_{h,l}(z,t)$ the molar holdup in the liquid phase per unit length.

Eq. (3.29) is subject to the following initial and advective boundary conditions:

$$\mathbf{c}_l^{\varepsilon}(z,0) = \mathbf{c}_{l,0}^{\varepsilon}(z), \quad \forall z > 0 \quad \text{(IC)},$$
$$\mathbf{c}_l^{\varepsilon}(0,t) = \mathbf{c}_{l,in}^{\varepsilon}(t), \quad \forall t \geq 0 \quad \text{(BC)}.$$

Furthermore, the system is subject to constraints related to the p_l intermediate inlet-

[2]Both the diffusion coefficients in liquids and the temperature gradients inside separation columns are relatively small.

s/outlets at the positions z_h[3]

$$\mathbf{c}_l^{\varepsilon}(z_h,t) = \mathbf{Z}_{in,h}\frac{\mathbf{f}_{in,h}}{q_l(z_h,t)} + \mathbf{c}_l^{\varepsilon}(z_h^-,t)\,\alpha_l(z_h,t), \quad \forall h = 1,\ldots,p_l, \quad \forall t \geq 0, \tag{3.30}$$

where $\alpha_l(z_h,t) := \frac{1}{v_{l,z}(z_h,t)}\left(v_{l,z}(z_h^-,t) - \frac{q_{out,h}(t)}{A_l(z_h^-,t)}\right)$, $\mathbf{f}_{in,h}(t)$ is the $p_{l,h}$-dimensional vector of molar flowrates of the liquid inlets at the hth intermediate column inlet/outlet, $\mathbf{Z}_{in,h}(t)$ is an $S_l \times p_{l,h}$ matrix, whose jth column $\mathbf{Z}_{in,h,j}(t)$ is the vector of molar fractions of the jth liquid inlet at the hth intermediate inlet/outlet, $q_l(z,t) := v_{l,z}(z,t)A$ is the volumetric flowrate in the column, $q_{out,h}(t)$ is the volumetric flowrate of the outlet at the hth intermediate inlet/outlet, and $A_l(z,t) := \varepsilon_l(z,t)A$ is the cross-section area occupied by the liquid phase.

3.4.1.2 Effect of advection and intermediate outlets on the IC and BC

The effect of advection and intermediate outlet flows on the initial and advective boundary conditions can be computed by solving Eq. (3.20), with the initial and boundary conditions given by Eqs. (3.21) and (3.22), replacing the subscript f by l. In addition, for the intermediate inlets/outlets at the positions z_h,

$$\mathbf{c}_{ibc,l}^{\varepsilon}(z_h,t) = \mathbf{Z}_{in,h}\frac{\mathbf{f}_{in,h}}{q_l(z_h,t)} + \mathbf{c}_{ibc,l}^{\varepsilon}(z_h^-,t)\,\alpha_l(z_h,t), \quad \forall h = 1,\ldots,p_l, \quad \forall t \geq 0.$$

3.4.1.3 Extents $\mathbf{x}_{r,l}(z,t)$ and $\mathbf{x}_{m,l}(z,t)$

The extent of reaction $x_{r,l,i}(z,t)$ represents the amount of material that has been processed by the ith reaction in phase L and is at position z at time t. These extents are described by Eq. (3.23), with the corresponding initial and boundary conditions, replacing the subscript f by l, and the constraints

$$\mathbf{x}_{r,l}(z_h,t) = \mathbf{x}_{r,l}(z_h^-,t)\,\alpha_l(z_h,t), \ \forall h = 1,\ldots,p_l, \ \forall t \geq 0.$$

The extent of mass transfer $x_{m,l,k}(z,t)$ represents the amount of material that has transferred to phase L via the kth mass transfer and is at position z at time t. These extents are described by Eq. (3.24), with the corresponding initial and boundary conditions, replacing the subscript f by l, and the constraints

$$\mathbf{x}_{m,l}(z_h,t) = \mathbf{x}_{m,l}(z_h^-,t)\,\alpha_l(z_h,t), \ \forall h = 1,\ldots,p_l, \ \forall t \geq 0.$$

[3] Eq. (3.30) results from the rearrangement of the material balance $\mathbf{c}_l^{\varepsilon}(z_h^-,t)q_l(z_h^-,t) + \mathbf{Z}_{in,h}\mathbf{f}_{in,h} = \mathbf{c}_l^{\varepsilon}(z_h,t)q_l(z_h,t) + \mathbf{c}_l^{\varepsilon}(z_h^-,t)\frac{q_{out,h}}{\varepsilon_l(z_h^-,t)}$ for $\mathbf{c}_l^{\varepsilon}(z_h,t)$, where z_h^- indicates the axial position right before the position of the hth intermediate column inlet/outlet.

Eq. (3.29) can be reconstructed from $\mathbf{c}^{\varepsilon}_{ibc,l}(z,t)$ and the extents of reaction $\mathbf{x}_{r,l}(z,t)$ and of mass transfer $\mathbf{x}_{m,l}(z,t)$ defined above using

$$\mathbf{c}^{\varepsilon}_{l} = \mathscr{L}_l \begin{bmatrix} \mathbf{x}_{r,l} \\ \mathbf{x}_{m,l} \end{bmatrix} + \mathbf{c}^{\varepsilon}_{ibc,l}, \tag{3.31}$$

with $\mathscr{L}_l = \begin{bmatrix} \mathbf{N}_l^{\mathrm{T}} & \mathbf{E}_{m,l} \end{bmatrix}$.

3.4.1.4 Transformation to extents

If $\mathrm{rank}(\mathscr{L}_l) = R_l + p_{m,l}$, the extents of reaction and mass transfer are given by the linear transformation

$$\begin{bmatrix} \mathbf{x}_{r,l} \\ \mathbf{x}_{m,l} \end{bmatrix} = \mathscr{T}_l \, \delta \mathbf{c}^{\varepsilon}_{l}, \tag{3.32}$$

with $\mathscr{T}_l := \left(\mathscr{L}_l^{\mathrm{T}} \mathbf{W} \mathscr{L}_l \right)^{-1} \mathscr{L}_l^{\mathrm{T}} \mathbf{W}$, and $\delta \mathbf{c}^{\varepsilon}_{l} := \mathbf{c}^{\varepsilon}_{l} - \mathbf{c}^{\varepsilon}_{ibc,l}$.

3.4.1.5 Combined material and heat balance equations

The combined material and heat balance equations are described in Appendix B.1.6.

3.4.2 Tray reactive separation columns

This section considers the case of a reactive separation column with N trays. It is often assumed for such columns that the liquid phase on each tray is perfectly mixed. Hence, the system of S_l PDEs in Eq. (3.29) simplifies to a system of $N \cdot S_l$ ODEs that depend on time only.

In the following, the equations are presented for a single tray, and the tray number $n = 1, \ldots, N$ replaces the variable z used for packed columns in Section 3.4.1. Also, the presence of inlet and outlet streams on the nth tray is handled by introducing the variables $\mathbf{Z}_{in,n}$, $\mathbf{f}_{in,n}$ and $q_{out,n}$ as in Section 3.4.1, replacing h by n.

3.4.2.1 Material balance equations, $\mathbf{n}_{l,n}(t)$

The S_l-dimensional vector of concentrations $\mathbf{c}^{\varepsilon}_{l,n}(t)$ on the nth tray is described by the ODE

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{c}^{\varepsilon}_{l,n} + \Delta^{\omega}\mathbf{c}^{\varepsilon}_{l,n} + \omega_{out,n}\,\mathbf{c}^{\varepsilon}_{l,n} &= \mathbf{N}_l^{\mathrm{T}}\mathbf{r}^{\varepsilon}_{l,n} + \mathbf{E}_{m,l}\boldsymbol{\phi}^{\varepsilon}_{m,l,n} + \mathbf{Z}_{in,n}\frac{\mathbf{f}_{in,n}}{V_{t,n}}, \\ \mathbf{c}^{\varepsilon}_{l,n}(0) &= \mathbf{c}^{\varepsilon}_{l,n,0}, \end{aligned} \tag{3.33}$$

where $\omega_{out,n}(t) := \frac{q_{out,n}(t)}{V_{l,n}(t)}$, with $V_{l,n}(t) := \varepsilon_{l,n}(t)\,V_{t,n}$ the volume of the liquid phase on the nth tray and $V_{t,n}$ the total volume on the nth tray. We define the operator Δ^{ω} applied to any variable $y_{l,n}$ as $\Delta^{\omega} y_{l,n} := \omega_{l,n} y_{l,n} - \omega_{l,n-1} y_{l,n-1}$, with $\omega_{l,n}(t) := \frac{L_n(t)}{n_{h,n}(t)}$, $L_n(t)$ the molar advective flowrate of the liquid phase that is transferred from the nth to the $(n+1)$st tray and $n_{h,n}(t)$ the molar holdup in the liquid phase of the nth tray.

Multiplying Eq. (3.33) by $V_{t,n}$ leads to an expression for $\mathbf{n}_{l,n}(t) := V_{t,n}\mathbf{c}^{\varepsilon}_{l,n}(t)$, the S_l-dimensional vector of numbers of moles on the nth tray

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{n}_{l,n} + \Delta^{\omega}\mathbf{n}_{l,n} + \omega_{out,n}\,\mathbf{n}_{l,n} &= \mathbf{N}_l^{\mathrm{T}}\mathbf{r}^{v}_{l,n} + \mathbf{E}_{m,l}\boldsymbol{\phi}^{v}_{m,l,n} + \mathbf{Z}_{in,n}\mathbf{f}_{in,n},\\ \mathbf{n}_{l,n}(0) &= \mathbf{n}_{l,n,0},\end{aligned} \tag{3.34}$$

with $\mathbf{r}^{v}_{l,n}(t) := V_{t,n}\,\mathbf{r}^{\varepsilon}_{l,n}(t)$, and $\boldsymbol{\phi}^{v}_{m,l,n}(t) := V_{t,n}\,\boldsymbol{\phi}^{\varepsilon}_{m,l,n}(t)$.

3.4.2.2 Effect of outlets and transfer between trays on the IC and IFC

The effect of the outlet flows and transfer of material between trays on the initial and inlet flow conditions can be computed as $\mathbf{n}_{iic,l,n}(t)$ by solving the ODE

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{n}_{iic,l,n} + \Delta^{\omega}\mathbf{n}_{iic,l,n} + \omega_{out,n}\,\mathbf{n}_{iic,l,n} &= \mathbf{Z}_{in,n}\mathbf{f}_{in,n},\\ \mathbf{n}_{iic,l,n}(0) &= \mathbf{n}_{l,n,0}.\end{aligned} \tag{3.35}$$

3.4.2.3 Extents $\mathbf{x}_{r,l,n}(t)$ and $\mathbf{x}_{m,l,n}(t)$

The extent of reaction $x_{r,l,n,i}(t)$ represents the amount of material that has been processed by the ith reaction in phase L and is on the nth tray at time t. These extents are described by the ODE

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{x}_{r,l,n} + \Delta^{\omega}\mathbf{x}_{r,l,n} + \omega_{out,n}\,\mathbf{x}_{r,l,n} &= \mathbf{r}^{v}_{l,n},\\ \mathbf{x}_{r,l,n}(0) &= \mathbf{0}_{R_l}.\end{aligned} \tag{3.36}$$

The extent of mass transfer $x_{m,l,n,k}(t)$ represents the amount of material that has transferred to phase L via the kth mass transfer and is on the nth tray at time t. These extents are described by the ODE

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{x}_{m,l,n} + \Delta^{\omega}\mathbf{x}_{m,l,n} + \omega_{out,n}\,\mathbf{x}_{m,l,n} &= \boldsymbol{\phi}^{v}_{m,l,n},\\ \mathbf{x}_{m,l,n}(0) &= \mathbf{0}_{p_{m,l}}.\end{aligned} \tag{3.37}$$

Eq. (3.34) can be reconstructed from $\mathbf{n}_{iic,l,n}(t)$ and the extents of reaction $\mathbf{x}_{r,l,n}(t)$ and

of mass transfer $\mathbf{x}_{m,l,n}(t)$ defined above using

$$\mathbf{n}_{l,n} = \mathscr{L}_l \begin{bmatrix} \mathbf{x}_{r,l,n} \\ \mathbf{x}_{m,l,n} \end{bmatrix} + \mathbf{n}_{iic,l,n}, \tag{3.38}$$

with $\mathscr{L}_l = \begin{bmatrix} \mathbf{N}_l^{\mathrm{T}} & \mathbf{E}_{m,l} \end{bmatrix}$.

3.4.2.4 Transformation to extents

If $\mathrm{rank}(\mathscr{L}_l) = R_l + p_{m,l}$, the extents of reaction and mass transfer are given by the linear transformation

$$\begin{bmatrix} \mathbf{x}_{r,l,n} \\ \mathbf{x}_{m,l,n} \end{bmatrix} = \mathscr{T}_l \, \delta\mathbf{n}_{l,n}, \tag{3.39}$$

with $\mathscr{T}_l := \left(\mathscr{L}_l^{\mathrm{T}} \mathbf{W} \mathscr{L}_l\right)^{-1} \mathscr{L}_l^{\mathrm{T}} \mathbf{W}$, and $\delta\mathbf{n}_{l,n} := \mathbf{n}_{l,n} - \mathbf{n}_{iic,l,n}$.

3.4.2.5 Combined material and heat balance equations

The combined material and heat balance equations are described in Appendix B.1.7.

3.5 Generic Distributed Reaction Systems

In a generic distributed reaction system with three dimensions and multiple phases (advection–diffusion–mass transfer–reaction problem), all quantities in each phase F can be written as functions of the three spatial coordinates $\boldsymbol{\chi} = (\chi_1, \chi_2, \chi_3)$ and the time t. Let us assume that the domain of $\mathbf{c}_f^{\varepsilon}(\boldsymbol{\chi}, t)$ is $\left\{(\boldsymbol{\chi}, t) : \boldsymbol{\chi} \in \mathscr{D} \subset \mathbb{R}^3 \wedge t \geq 0\right\}$. The initial conditions (for $t = 0$) are in the set $IC = \mathrm{int}(\mathscr{D})$, whereas the boundary conditions (for all $t \geq 0$) are in the set $BC = \partial(\mathscr{D})$.

For all $\boldsymbol{\chi} \in BC$, $\vec{\mathbf{n}}(\boldsymbol{\chi})$ is the inward-pointing vector normal to $\mathscr{D}$ at $\boldsymbol{\chi}$. The *advective* boundary conditions are in the set $aBC = \left\{\boldsymbol{\chi} \in BC : \mathbf{v}_f^{\mathrm{T}}(\boldsymbol{\chi}, t)\vec{\mathbf{n}}(\boldsymbol{\chi}) > 0\right\}$, with $\mathbf{v}_f$ the vector of advective velocities, while the *diffusive* boundary conditions are in the set $dBC = \left\{\boldsymbol{\chi} \in BC : \mathbf{v}_f^{\mathrm{T}}(\boldsymbol{\chi}, t)\vec{\mathbf{n}}(\boldsymbol{\chi}) \leq 0\right\}$.

3.5.1 Simplifications for specific reaction systems

For a specific reaction system, relevant assumptions allow simplifying the generic case described above. The relevant simplifications are shown below for some of the systems described in the previous sections.

3.5.1.1 Packed reactive separation columns

For a packed column, $\boldsymbol{\chi}$ reduces to the single spatial coordinate z. Advection is only in the axial direction and, since there is perfect mixing at each axial position and no axial diffusion, there is no radial diffusion and $\mathbf{c}_f^\varepsilon$ and $v_{f,z}$ are functions of z and t. With the top of the column located at $z = 0$ and z being positive inside the column, the domain is $\mathscr{D} = \{z : z \geq 0\}$. The initial conditions are given for all positions $z > 0$, and the *advective* boundary conditions are given at $z = 0$, for $t \geq 0$.

3.5.1.2 Multiphase two-dimensional tubular reactors

For a two-dimensional tubular reactor of radius $\mathscr{R}$, $\boldsymbol{\chi}$ reduces to the cylindrical coordinates z and r. Advection is only in the axial direction, and $\mathbf{c}_f^\varepsilon$ and $v_{f,z}$ are functions of z, r and t. With the reactor inlet located at $z = 0$ and z being positive inside the reactor, the domain is $\mathscr{D} = \{(z,r) : z \geq 0 \wedge r \in [0,\mathscr{R}]\}$. The initial conditions are given for all positions $z > 0$ and $r \in]0,\mathscr{R}[$. The *advective* boundary conditions are given at the inlet position $z = 0$, for $r \in]0,\mathscr{R}[$ and $t \geq 0$. The *diffusive* boundary conditions are given at the center, where $r = 0$, for $z \geq 0$ and $t \geq 0$, at the walls, where $r = \mathscr{R}$, for $z \geq 0$ and $t \geq 0$, and at the end of the (infinite) reactor, where $z \to \infty$, for $r \in]0,\mathscr{R}[$ and $t \geq 0$.

3.5.1.3 Multiphase one-dimensional tubular reactors

For a one-dimensional tubular reactor, $\boldsymbol{\chi}$ reduces to the spatial coordinate z. Since there is perfect mixing at each axial position, there is no radial diffusion and $\mathbf{c}_f^\varepsilon$ and $v_{f,z}$ are functions of z and t. The domain reduces to $\mathscr{D} = \{z : z \geq 0\}$. The initial conditions are given for all positions $z > 0$. The *advective* boundary conditions are given at the inlet position $z = 0$, for $t \geq 0$, while the *diffusive* boundary conditions are given at the end of the (infinite) reactor, where $z \to \infty$, for $t \geq 0$.

3.5.1.4 Single-phase one-dimensional tubular reactors

For a single-phase one-dimensional tubular reactor, (i) there are no mass-transfer terms, and (ii) the concentrations read $\mathbf{c}(z,t)$ and the velocity $v_z(z,t)$. For the rest, the situation is the same as for the aforementioned multiphase one-dimensional case.

3.5.2 Material balance equations, $\mathbf{c}_f^\varepsilon(\boldsymbol{\chi},t)$

The concentrations $\mathbf{c}_f^\varepsilon(\boldsymbol{\chi},t)$ are described by the PDE[4]

$$\frac{\partial}{\partial t}\mathbf{c}_f^\varepsilon + \nabla\cdot\left(\mathbf{v}_f\mathbf{c}_f^{\varepsilon\,\mathrm{T}}\right) = \mathbf{N}_f^{\mathrm{T}}\mathbf{r}_f^\varepsilon + \mathbf{E}_{m,f}\boldsymbol{\phi}_{m,f}^\varepsilon + \mathbf{E}_{d,f}\boldsymbol{\phi}_{d,f}^\varepsilon. \tag{3.40}$$

[4]For any two vectors $\mathbf{v}$ and $\mathbf{y}$, the definition $\nabla\cdot(\mathbf{v}\mathbf{y}^{\mathrm{T}}) := (\nabla\cdot\mathbf{v})\mathbf{y} + (\mathbf{v}\cdot\nabla)\mathbf{y}$ is used throughout this section.

The existence of diffusion in all three coordinates $\boldsymbol{\chi}$ requires defining a matrix of diffusion fluxes of dimension $p_d \times 3$, denoted $\mathbf{J}^{\varepsilon}_{d,f}(\boldsymbol{\chi},t)$, which is described by the PDE

$$\nabla \cdot \mathbf{J}^{\varepsilon\,\mathrm{T}}_{d,f,j} = -\phi^{\varepsilon}_{d,f,j}, \quad \forall j = 1,\ldots,p_d, \tag{3.41}$$

with the diffusive boundary conditions

$$\mathbf{J}^{\varepsilon}_{d,f}(\boldsymbol{\chi},t)\,\vec{\mathbf{n}}(\boldsymbol{\chi}) = \mathbf{0}_{p_{d,f}},\ \forall \boldsymbol{\chi} \in dBC,\ \forall t \geq 0.$$

Eq. (3.40) is subject to the following initial and advective boundary conditions:

$$\begin{aligned}
&\mathbf{c}^{\varepsilon}_{f}(\boldsymbol{\chi},0) = \mathbf{c}^{\varepsilon}_{f,0}(\boldsymbol{\chi}), && \forall \boldsymbol{\chi} \in IC && \text{(IC)},\\
&\mathbf{c}^{\varepsilon}_{f}(\boldsymbol{\chi},t) = \mathbf{c}^{\varepsilon}_{f,in}(\boldsymbol{\chi},t) + \mathbf{c}^{\varepsilon}_{d,f}(\boldsymbol{\chi},t), && \forall \boldsymbol{\chi} \in aBC, \forall t \geq 0 && \text{(BC)},
\end{aligned}$$

with $\mathbf{c}^{\varepsilon}_{d,f}(\boldsymbol{\chi},t) := -\frac{\mathbf{E}_{d,f}\mathbf{J}^{\varepsilon}_{d,f}(\boldsymbol{\chi},t)\,\vec{\mathbf{n}}(\boldsymbol{\chi})}{\beta \mathbf{v}_f(\boldsymbol{\chi},t)^{\mathrm{T}}\vec{\mathbf{n}}(\boldsymbol{\chi})}$. These initial and boundary conditions are also affected by those of Eq. (3.41).

3.5.3 Effect of advection on the IC and BC

The effect of advection on the initial and advective boundary conditions can be computed as $\mathbf{c}^{\varepsilon}_{ibc,f}(\boldsymbol{\chi},t)$ by solving the PDE

$$\frac{\partial}{\partial t}\mathbf{c}^{\varepsilon}_{ibc,f} + \nabla \cdot \left(\mathbf{v}_f \mathbf{c}^{\varepsilon\,\mathrm{T}}_{ibc,f}\right) = \mathbf{0}_{S_f}, \tag{3.42}$$

with the initial and boundary conditions

$$\begin{aligned}
&\mathbf{c}^{\varepsilon}_{ibc,f}(\boldsymbol{\chi},0) = \mathbf{c}^{\varepsilon}_{f,0}(\boldsymbol{\chi}), && \forall \boldsymbol{\chi} \in IC && \text{(IC)},\\
&\mathbf{c}^{\varepsilon}_{ibc,f}(\boldsymbol{\chi},t) = \mathbf{c}^{\varepsilon}_{f,in}(\boldsymbol{\chi},t), && \forall \boldsymbol{\chi} \in aBC,\ \forall t \geq 0 && \text{(BC)}.
\end{aligned}$$

3.5.4 Extents $\mathbf{x}_{r,f}(\boldsymbol{\chi},t)$, $\mathbf{x}_{m,f}(\boldsymbol{\chi},t)$ and $\mathbf{x}_{d,f}(\boldsymbol{\chi},t)$

The extent of reaction $x_{r,f,i}(\boldsymbol{\chi},t)$ represents the amount of material that has been processed by the ith reaction in phase F and is at position $\boldsymbol{\chi}$ at time t. These extents are described by the PDE

$$\frac{\partial}{\partial t}\mathbf{x}_{r,f} + \nabla \cdot \left(\mathbf{v}_f \mathbf{x}^{\mathrm{T}}_{r,f}\right) = \mathbf{r}^{\varepsilon}_{f}, \tag{3.43}$$

with $\mathbf{x}_{r,f}(\boldsymbol{\chi},0) = \mathbf{0}_{R_f},\ \forall \boldsymbol{\chi} \in IC$ (IC), and $\mathbf{x}_{r,f}(\boldsymbol{\chi},t) = \mathbf{0}_{R_f},\ \forall \boldsymbol{\chi} \in aBC,\ \forall t \geq 0$ (BC).

The extent of mass transfer $x_{m,f,k}(\boldsymbol{\chi},t)$ represents the amount of material that has transferred to phase F via the kth mass transfer and is at position $\boldsymbol{\chi}$ at time t. These extents are

described by the PDE

$$\frac{\partial}{\partial t}\mathbf{x}_{m,f} + \nabla \cdot \left(\mathbf{v}_f \mathbf{x}_{m,f}^{\mathrm{T}}\right) = \boldsymbol{\phi}_{m,f}^{\varepsilon}, \tag{3.44}$$

with $\mathbf{x}_{m,f}(\boldsymbol{\chi},0) = \mathbf{0}_{p_{m,f}}$, $\forall\, \boldsymbol{\chi} \in IC$ (IC) and $\mathbf{x}_{m,f}(\boldsymbol{\chi},t) = \mathbf{0}_{p_{m,f}}$, $\forall \boldsymbol{\chi} \in aBC$, $\forall t \geq 0$ (BC).

The extent of diffusion $x_{d,f,j}(\boldsymbol{\chi},t)$ represents the amount of material that has transferred via the jth diffusion rate in phase F and is at position $\boldsymbol{\chi}$ at time t. These extents are described by the PDE

$$\frac{\partial}{\partial t}\mathbf{x}_{d,f} + \nabla \cdot \left(\mathbf{v}_f \mathbf{x}_{d,f}^{\mathrm{T}}\right) = \boldsymbol{\phi}_{d,f}^{\varepsilon}, \tag{3.45}$$

with $\mathbf{x}_{d,f}(\boldsymbol{\chi},0) = \mathbf{0}_{p_{d,f}}$, $\forall \boldsymbol{\chi} \in IC$ (IC), and $\mathbf{x}_{d,f}(\boldsymbol{\chi},t) = -\frac{\mathbf{J}_{d,f}^{\varepsilon}(\boldsymbol{\chi},t)\vec{\mathbf{n}}(\boldsymbol{\chi})}{\beta \mathbf{v}_f(\boldsymbol{\chi},t)^{\mathrm{T}}\vec{\mathbf{n}}(\boldsymbol{\chi})}$, $\forall \boldsymbol{\chi} \in aBC$, $\forall t \geq 0$ (BC).

Eq. (3.40) can be reconstructed from Eqs. (3.42)-(3.45) using Eq. (3.26).

3.5.5 Transformation to extents

If rank $\left(\mathscr{L}_f\right) = R_f + p_{m,f} + p_{d,f}$, the extents of reaction, mass transfer and diffusion are given by the linear transformation in Eq. (3.27).

3.5.6 Combined material and heat balance equations

The combined material and heat balance equations are described in Appendix B.1.8.

3.6 Case Studies

This section shows the application of the transformation to extents to four examples of distributed reaction systems, namely, a single-phase plug-flow reactor (without diffusion), a single-phase one-dimensional tubular reactor (with diffusion), a packed reactive absorption column, and a tray reactive distillation column. The purpose of these case studies is to illustrate the concept of extents and how these extents can be computed in specific cases. The discussion about the possible applications of the concept of extents in distributed reaction systems is postponed to the final section of this chapter, although the results in this section may already reveal that the decoupling of rate processes provided by the transformation to extents is helpful for monitoring and fault diagnosis.

3.6.1 Single-phase plug-flow reactor

Let us consider the plug-flow reactor with a single fluid phase discussed in Section 3.2.2. The liquid phase consists of solvent and the species A, B, C and D that are involved in the $R = 2$ reactions A + B $\rightarrow$ C and 2B $\rightarrow$ D. For this system, the vector of concentrations is

$\mathbf{c} = \begin{bmatrix} c_A & c_B & c_C & c_D \end{bmatrix}^{\mathrm{T}}$, and the stoichiometric matrix is $\mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 0 \\ 0 & -2 & 0 & 1 \end{bmatrix}$.

Initially, the reactor contains only solvent and the species A with a concentration starting at 2 mol L^{-1} and decreasing exponentially along the reactor length. This defines the IC as $\mathbf{c}_0(z) = \begin{bmatrix} 2 & 0 & 0 & 0 \end{bmatrix}^{\mathrm{T}} \exp(-2z)$, $\forall z > 0$, which is useful to demonstrate that the concept of extents and the linear transformation to extents can deal with arbitrary initial conditions[5]. The reactor is fed with a mixture of solvent and species A and B with concentrations 2 and 1.5 mol L^{-1}, respectively. This defines the advective BC as $\mathbf{c}_{in}(t) = \begin{bmatrix} 2 & 1.5 & 0 & 0 \end{bmatrix}^{\mathrm{T}}$ mol L^{-1}, $\forall t \geq 0$. The velocity along the z-direction is assumed to be constant at $v_z = 1.25$ m s^{-1}. The reaction rates are given by the following kinetic laws:

$$r_1 = k_1 c_A c_B, \tag{3.46}$$

$$r_2 = k_2 c_B^2, \tag{3.47}$$

with $k_1 = 0.1$ L mol^{-1} s^{-1}, $k_2 = 0.3$ L mol^{-1} s^{-1} for a constant temperature.

Figure 3.1 shows the concentrations c_A, c_B, c_C and c_D simulated with Eq. (3.6) for $z \in [0, 1]$ m and $t \in \{0, 0.1, \ldots, 0.8\}$ s (thin gray lines) and the steady state that is reached when $t \to \infty$ (thick black line). Figure 3.2 shows the corresponding profiles of the variables δc_A and δc_B. Since C and D are not initially present and are not fed through the inlet, $c_{ibc,C}$ and $c_{ibc,D}$ are identically equal to zero and δc_C and δc_D are equal to c_C and c_D. The extents of reaction $x_{r,1}$ and $x_{r,2}$ in Figure 3.2 are computed using the linear transformation of Eq. (3.12) from $\delta\mathbf{c}$. In this case, $\mathscr{T}$ exists because $\mathrm{rank}(\mathscr{L}) = R = 2$, where $\mathscr{L} = \mathbf{N}^{\mathrm{T}}$. However, even if this rank condition were not satisfied, one could compute the extents via integration of Eq. (3.10) with the kinetic laws of Eqs. (3.46)–(3.47).

In Figures 3.1 and 3.2, one can observe that, as time increases, the initial conditions are propagated toward the end of the reactor, while all the variables reach their steady-state values upstream of the propagation wave of the inlet conditions.

The situation is slightly different when there is diffusion, which makes the sharp transitions caused by the propagation wave of the inlet conditions become smoother, as shown next for the case of a single-phase one-dimensional tubular reactor.

3.6.2 Single-phase one-dimensional tubular reactor

Let us now assume that the $p_d = 2$ species A and B diffuse, which results in the diffusion matrix $\mathbf{E}_d = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}^{\mathrm{T}}$. We have the situation of the single-phase one-dimensional tubular reactor discussed in Section 3.3.1.

The reaction rates are given by Eqs. (3.46)–(3.47), while the diffusion rates obey the

[5] These initial conditions can be interpreted physically as the result of a change of conditions at time $t = 0$, with the conditions before $t = 0$ being caused by a first-order reaction.

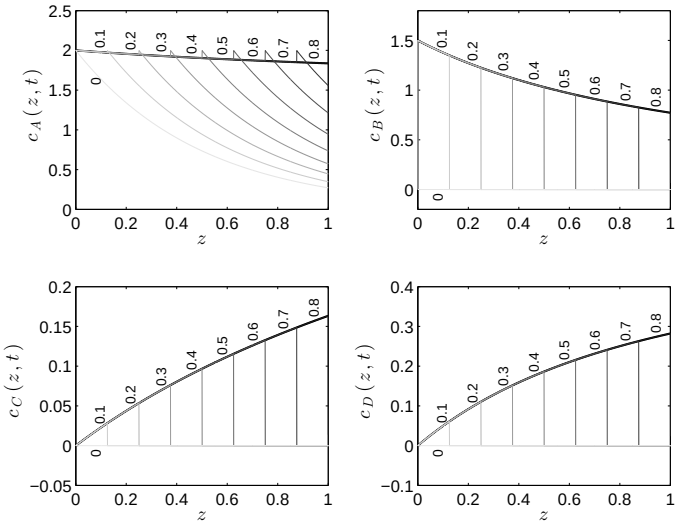

Figure 3.1 – Concentrations $\mathbf{c}(z,t)$ in mol L^{-1} along the z axis (in m) of a plug-flow reactor for different times in s (gray lines). The thick black lines indicate concentrations at steady state.

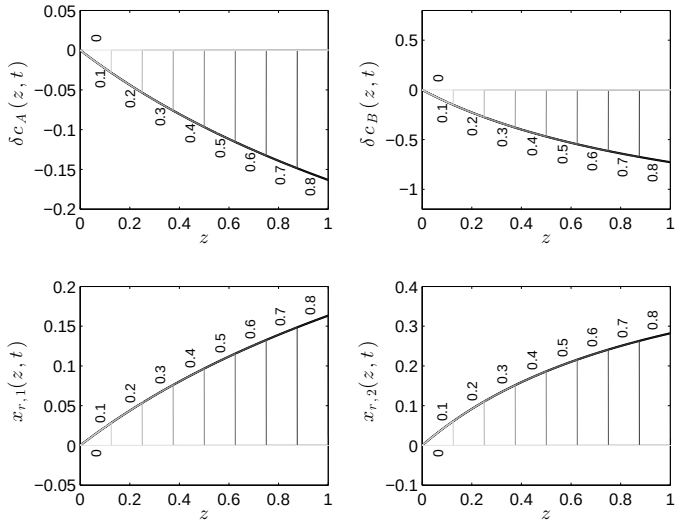

Figure 3.2 – Concentrations $\delta\mathbf{c}(z,t)$ and extents of reaction $\mathbf{x}_r(z,t)$ in mol L^{-1} along the z axis (in m) of a plug-flow reactor for different times in s (gray lines). The thick black lines indicate concentrations and extents at steady state.

following kinetic laws:

$$\phi_{d,A} = D_A \frac{\partial^2 c_A}{\partial z^2}, \tag{3.48}$$

$$\phi_{d,B} = D_B \frac{\partial^2 c_B}{\partial z^2}, \tag{3.49}$$

with $D_A = 1 \times 10^{-4}$ m^2 s^{-1} and $D_B = 5 \times 10^{-4}$ m^2 s^{-1} for a constant temperature.

Figure 3.3 shows the concentrations c_A, c_B, c_C and c_D simulated with Eq. (3.13) for $z \in [0,1]$ m and $t \in \{0, 0.1, \ldots, 0.8\}$ s (thin gray lines) and the steady state that is reached when $t \to \infty$ (thick black line). Figure 3.4 shows the corresponding profiles of the variables $c_{ibc,A}$, $c_{ibc,B}$, computed via Eq. (3.7) and equal to those that would be found for the previous plug-flow reactor, and the variables δc_A and δc_B. Since C and D are not initially present and are not fed through the inlet, $c_{ibc,C}$ and $c_{ibc,D}$ are identically equal to zero and δc_C and δc_D are equal to c_C and c_D. The extents of reaction $x_{r,1}$ and $x_{r,2}$ and of diffusion $x_{d,A}$ and $x_{d,B}$ in Figure 3.5 are computed using the linear transformation of Eq. (3.17) from $\delta\mathbf{c}$. In this case, $\mathscr{T}$ exists because $\text{rank}(\mathscr{L}) = R + p_d = 2 + 2 = 4$, where $\mathscr{L} = \begin{bmatrix}\mathbf{N}^{\mathrm{T}} & \mathbf{E}_d\end{bmatrix}$. However, even if this rank condition were not satisfied, one could compute the extents via integration of Eqs. (3.10) and (3.15) with the kinetic laws of Eqs. (3.46)–(3.49).

Figures 3.3–3.5 show that, besides the effects of reaction and advective propagation of the inlet conditions, already seen in Figures 3.1–3.2, the concentrations are also affected by diffusion, which becomes more visible at later times. The effect of diffusion is captured by the extents of diffusion that clearly indicate that diffusion affects the concentrations of A and B upstream and downstream of the propagation wave of the inlet conditions. For example, since the inlet contains B but the initial content of the reactor does not, the effect of diffusion decreases the concentration of B upstream of the propagation wave (from the high value associated with the boundary conditions) and increases it downstream (from the zero value of the initial conditions). This effect causes a negative value of $x_{d,B}$ upstream and a positive value downstream of the propagation wave of the inlet conditions.

3.6.3 Packed reactive absorption column

Let us consider the reactive absorption column discussed in Section 3.4.1. The column, with a length of 4 m and an area $A = 1$ m^3, contains a liquid phase consisting of solvent S and the species A, B, C and D that are involved in the reversible reaction A + B $\leftrightharpoons$ C + D ($R_l = 1$). The column also contains a gas phase that is used to absorb species D ($p_{m,l} = 1$), the objective being here to produce the desired species C and remove the by-product D. The vector of concentrations in the liquid phase is $\mathbf{c}_l^\varepsilon = \begin{bmatrix} c_{l,A}^\varepsilon & c_{l,B}^\varepsilon & c_{l,C}^\varepsilon & c_{l,D}^\varepsilon & c_{l,S}^\varepsilon \end{bmatrix}^{\mathrm{T}}$, the stoichiometric matrix is $\mathbf{N}_l = \begin{bmatrix} -1 & -1 & 1 & 1 & 0 \end{bmatrix}$, and the mass-transfer matrix is $\mathbf{E}_{m,l} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 \end{bmatrix}^{\mathrm{T}}$.

Initially, the liquid phase contains 2.0 mol L^{-1} of A, 1.3 mol L^{-1} of B and 8.0 mol L^{-1} of solvent, so that the IC are $\mathbf{c}_{l,0}^\varepsilon(z) = \begin{bmatrix} 2.0 & 1.3 & 0 & 0 & 8.0 \end{bmatrix}^{\mathrm{T}}$ mol L^{-1}, $\forall z \in [0,4]$ m. The column is fed from the bottom ($z = 4$ m) with the constant flowrate $G = 20$ mol s^{-1} of pure absorbing

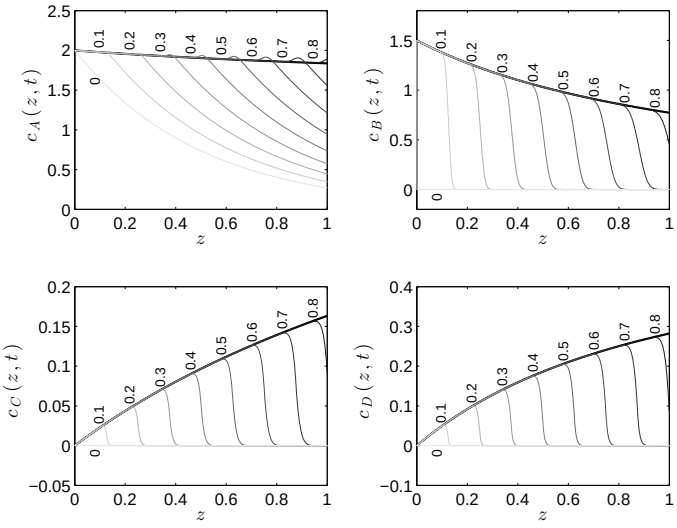

Figure 3.3 – Concentrations $\mathbf{c}(z,t)$ in mol L^{-1} along the z axis (in m) of a tubular reactor for different times in s (gray lines). The thick black lines indicate concentrations at steady state.

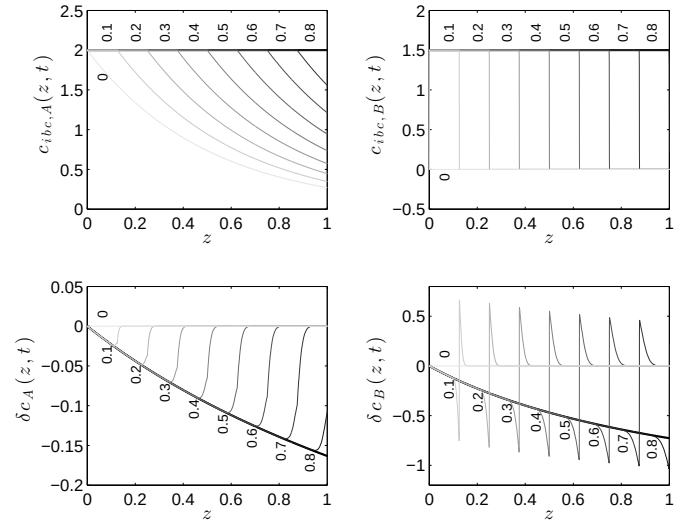

Figure 3.4 – Concentrations $\mathbf{c}_{ibc}(z,t)$ and $\delta\mathbf{c}(z,t)$ in mol L^{-1} along the z axis (in m) of a tubular reactor for different times in s (gray lines). The thick black lines indicate concentrations at steady state.

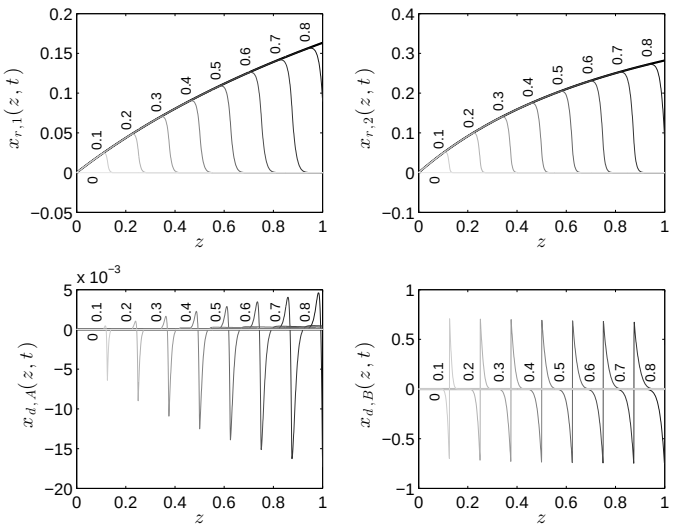

Figure 3.5 – Extents of reaction $\mathbf{x}_r(z,t)$ and of diffusion $\mathbf{x}_d(z,t)$ in mol L^{-1} along the z axis (in m) of a tubular reactor for different times in s (gray lines). The thick black lines indicate extents at steady state.

gas. The column is also fed from the top ($z = 0$ m) with a liquid at the constant flowrate $f_{in} = 113$ mol s^{-1} and the constant velocity $v_{l,z}(0,t) = 0.01$ m s^{-1}, $\forall t \geq 0$. The composition $\mathbf{Z}_{in}$ is constant and equal to that of $\mathbf{c}^{\varepsilon}_{l,0}$. This results in BC corresponding to the constant inlet concentration $\mathbf{c}^{\varepsilon}_{l,in}(t) = \mathbf{Z}_{in}\frac{f_{in}}{Av_{l,z}(0,t)}$, $\forall t \geq 0$. The molar liquid flowrate $L(z,t)$ is such that the volumetric fraction $\epsilon_l(z,t)$ remains constant at each position. Figure 3.6 sketches this reactive separation column.

The composition of the gas phase, given by the molar fractions $\mathbf{y}(z,t)$, is such that the gas phase at positions $z = 0$ m, $z = 0.05$ m, ..., $z = 3.95$ m is in equilibrium with the liquid phase in the sections $z \in]0, 0.05]$ m, $z \in]0.05, 0.1]$ m, ..., $z \in]3.95, 4]$ m. This equilibrium is given for species D by the equilibrium curve $y_D = K_D\, x_D$, with the coefficient $K_D = 10$ and the molar fraction of D in the liquid phase x_D. Assuming that the molar gas flowrate G is the same along the column and there is no accumulation of gas at any position, the mass-transfer rate reads

$$\phi^{\varepsilon}_{m,l} = \frac{G}{A}\frac{\partial}{\partial z} y_D. \tag{3.50}$$

The reaction rate is given by the following kinetic law:

$$r^{\varepsilon}_{l} = k_1 \frac{c^{\varepsilon}_{l,A} c^{\varepsilon}_{l,B}}{\varepsilon_l} - k_2 \frac{c^{\varepsilon}_{l,C} c^{\varepsilon}_{l,D}}{\varepsilon_l}, \tag{3.51}$$

with $k_1 = 2.18 \times 10^{-3}$ L mol^{-1} s^{-1} and $k_2 = 2.18 \times 10^{-4}$ L mol^{-1} s^{-1} for a constant

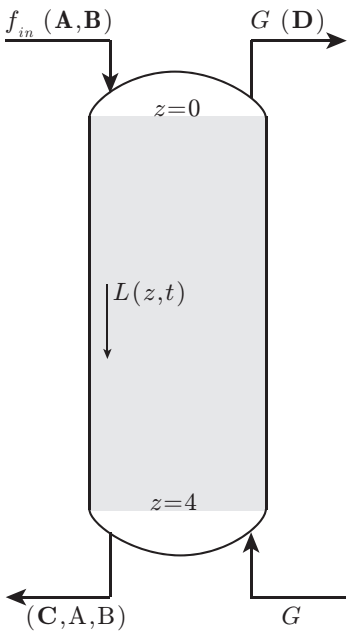

Figure 3.6 – Schematic of the packed reactive absorption column described in Section 3.6.3. The species present in the streams that enter and leave the column are shown in parentheses, with bold font used for the predominant species in each stream.

temperature.

Figure 3.7 shows the concentrations $c^{\varepsilon}_{l,A}$, $c^{\varepsilon}_{l,B}$, $c^{\varepsilon}_{l,C}$ and $c^{\varepsilon}_{l,D}$ simulated with Eq. (3.29) for $t \in [0,25]$ min and $z \in \{0, 0.3, 0.6, 1.0, 1.6, 2.2, 3.0, 4.0\}$ m. Figure 3.8 shows the corresponding profiles of the variables $\delta c^{\varepsilon}_{l,A}$ and $\delta c^{\varepsilon}_{l,B}$. Since C and D are not initially present and are not fed through the liquid inlet, $c^{\varepsilon}_{ibc,l,C}$ and $c^{\varepsilon}_{ibc,l,D}$ are identically equal to zero and $\delta c^{\varepsilon}_{l,C}$ and $\delta c^{\varepsilon}_{l,D}$ are equal to $c^{\varepsilon}_{l,C}$ and $c^{\varepsilon}_{l,D}$. The extents of reaction $x_{r,l,1}$ and of mass transfer $x_{m,l,D}$ in Figure 3.8 are computed using the linear transformation of Eq. (3.32) from $\delta \mathbf{c}^{\varepsilon}_{l}$. The linear transformation to extents exists because $\operatorname{rank}\left(\mathscr{L}_l\right) = R_l + p_{m,l} = 1 + 1 = 2$, where $\mathscr{L}_l = \left[\mathbf{N}_l^{\mathrm{T}} \;\; \mathbf{E}_{m,l}\right]$. However, even if this rank condition were not satisfied, one could compute the extents via integration of Eqs. (3.23) and (3.24), replacing the subscript f by l, with the kinetic laws of Eqs. (3.50) and (3.51).

The extents in Figure 3.8 show the cumulative effect of each rate process as a function of time for various positions in the column. The value of the extent of reaction is larger at the bottom than at higher positions, which can be easily explained by the fact that the reaction proceeds as the liquid flows down the column. The extent of mass transfer is positive near the top and negative near the bottom. Indeed, near the top, the species D transfers from the gas phase leaving the column, which is rich in D, to the liquid phase entering the column, which is poor in D; near the bottom, D transfers from the liquid phase leaving the column and rich in D to the gas phase entering the column and low in D. These effects are more difficult to interpret if one considers the concentrations in Figure 3.7.

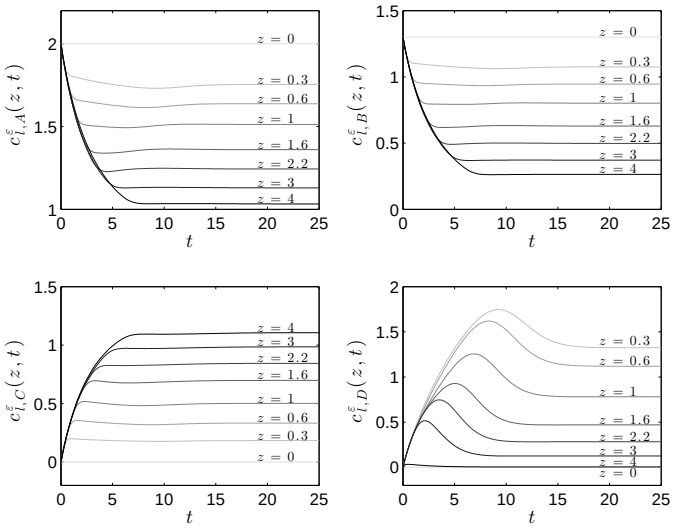

Figure 3.7 – Concentrations $\mathbf{c}_l^{\varepsilon}(z,t)$ in mol L^{-1} over time (in min) of a packed reactive absorption column for different positions z (in m).

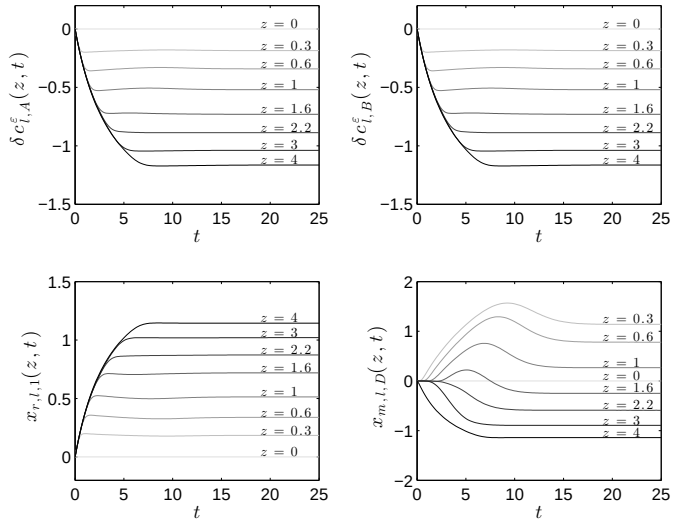

Figure 3.8 – Concentrations $\delta\mathbf{c}_l^{\varepsilon}(z,t)$ in mol L^{-1} and extents of reaction $x_{r,l}(z,t)$ and of mass transfer $x_{m,l}(z,t)$ in mol L^{-1} over time (in min) of a packed reactive absorption column for different positions z (in m).

3.6.4 Tray reactive distillation column

Let us consider the reactive distillation column discussed in Section 3.4.2. The column has $N = 4$ trays and the liquid phase consists of solvent S and the species A, B, C, D and E involved in the $R_l = 2$ reactions A + B → C + D and 2A + B → 2D + E. On each tray, the species A, D and S transfer between the liquid and vapor phases ($p_{m,l} = 3$). The vector of numbers of moles in the liquid phase on the nth tray is $\mathbf{n}_{l,n} = \left[\, n_{l,n,A} \; n_{l,n,B} \; n_{l,n,C} \; n_{l,n,D} \; n_{l,n,E} \; n_{l,n,S} \,\right]^{\mathrm{T}}$, the stoichiometric matrix is $\mathbf{N}_l = \begin{bmatrix} -1 & -1 & 1 & 1 & 0 & 0 \\ -2 & -1 & 0 & 2 & 1 & 0 \end{bmatrix}$, and the mass-transfer matrix is $\mathbf{E}_{m,l} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}^{\mathrm{T}}$.

Initially, the liquid phase on each tray contains 100 kmol of S and 13 kmol of B, which defines the IC as $\mathbf{n}_{l,n,0} = \left[\, 0 \; 13 \; 0 \; 0 \; 0 \; 100 \,\right]^{\mathrm{T}}$, $\forall n = 1, \ldots, N$. The column is fed from the bottom ($n = 4$) with the constant vapor flowrate $G = 20$ mol s^{-1} of pure A, and from the top ($n = 1$) with the constant liquid flowrate $f_{in,1} = 113$ mol s^{-1} of the same composition as $\mathbf{n}_{l,n,0}$. The molar liquid flowrates L_n between the trays are such that the liquid volume on each tray remains constant. At the top of the column ($n = 1$), the vapor goes through a condenser (with no accumulation), and $r = 5$ mol s^{-1} is recycled to the liquid phase on tray $n = 1$. Figure 3.9 sketches this reactive distillation column.

The composition of the vapor phase on the nth tray, given by the molar fractions $\mathbf{y}_n$, is such that the vapor phase is in equilibrium with the liquid phase on that tray. For each species s, with $s \in \{\mathrm{A}, \mathrm{B}, \mathrm{C}, \mathrm{D}, \mathrm{E}, \mathrm{S}\}$, this equilibrium is given by Raoult's law, $y_{n,s} P = x_{n,s} p_s^*$, with P the total pressure, $x_{n,s}$ the molar fraction of the species s in the liquid phase on the nth tray, and $p_A^* = 14.496$ bar, $p_D^* = 79.432$ bar and $p_S^* = 0.292$ bar the vapor pressures. Assuming that the molar vapor flowrate G between the trays is the same along the column and there is no accumulation of vapor on trays, the mass-transfer rates are given by

$$\boldsymbol{\phi}^v_{m,l,n} = \begin{cases} r\,\mathbf{y}_n + G\left(\mathbf{y}_{n+1} - \mathbf{y}_n\right), & n = 1 \\ G\left(\mathbf{y}_{n+1} - \mathbf{y}_n\right), & n = 2, \ldots, N. \end{cases} \tag{3.52}$$

Note that, due to the vapor feed of pure A at the bottom of the column, $\mathbf{y}_{N+1} = \left[\, 1 \; 0 \; 0 \; 0 \; 0 \; 0 \,\right]^{\mathrm{T}}$. The reaction rates are given by the following kinetic laws:

$$r^v_{l,n,1} = V_{l,n}\, k_1 \left(\frac{n_{l,n,A}}{V_{l,n}}\right)\left(\frac{n_{l,n,B}}{V_{l,n}}\right), \tag{3.53}$$

$$r^v_{l,n,2} = V_{l,n}\, k_2 \left(\frac{n_{l,n,A}}{V_{l,n}}\right)^2\left(\frac{n_{l,n,B}}{V_{l,n}}\right), \tag{3.54}$$

with $k_1 = 2.18 \times 10^{-3}$ L mol^{-1} s^{-1} and $k_2 = 2.18 \times 10^{-4}$ L^2 mol^{-2} s^{-1} for a constant temperature.

Figure 3.10 shows the numbers of moles $n_{l,n,A}$, $n_{l,n,B}$, $n_{l,n,C}$ and $n_{l,n,D}$ simulated with Eq. (3.34) for $t \in [0, 250]$ min and each of the 4 trays, $n = 1, \ldots, 4$. Since A, C and D are not initially present and are not fed through the liquid inlet, $n_{iic,l,n,A}$, $n_{iic,l,n,C}$ and $n_{iic,l,n,D}$

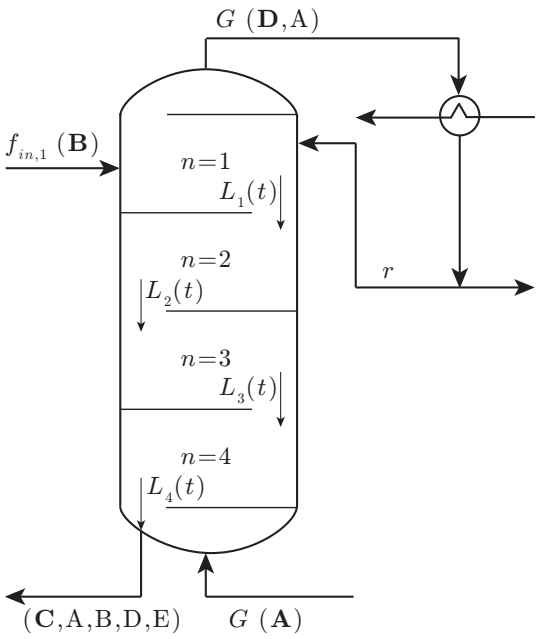

Figure 3.9 – Schematic of the tray reactive distillation column described in Section 3.6.4. The species present in the streams that enter and leave the column are shown in parentheses, with bold font used for the predominant species in each stream.

are identically equal to zero and $\delta n_{l,n,A}$, $\delta n_{l,n,C}$ and $\delta n_{l,n,D}$ are equal to $n_{l,n,A}$, $n_{l,n,C}$ and $n_{l,n,D}$. The quantities $\delta n_{l,n,B}$ have a shape similar to $n_{l,n,B}$, as $n_{iic,l,n,B}$ remain approximately equal to the initial conditions $n_{l,n,B,0}$ (results not shown). The extents of reaction $x_{r,l,n,1}$ and $x_{r,l,n,2}$ and of mass transfer $x_{m,l,n,A}$ and $x_{m,l,n,D}$ in Figure 3.11 are computed using the linear transformation of Eq. (3.39) from $\delta \mathbf{n}_{l,n}$. The linear transformation to extents exists because $\text{rank}\left(\mathscr{L}_l\right) = R_l + p_{m,l} = 2 + 3 = 5$, where $\mathscr{L}_l = \left[\mathbf{N}_l^{\mathrm{T}} \;\; \mathbf{E}_{m,l}\right]$. However, even if this rank condition were not satisfied, one could compute the extents via integration of Eqs. (3.36) and (3.37) with the kinetic laws of Eqs. (3.52)–(3.54).

The extents in Figure 3.11 show the cumulative effect of each rate process as a function of time for each tray. For all extents, the magnitude on the tray $n = 4$ (from the top) is larger than on higher trays, because the extents on each tray take into account the effect of the corresponding rate processes on the trays from the top to that tray. These effects are more difficult to interpret if one considers the numbers of moles in Figure 3.10.

3.7 Conclusion

This chapter has provided a novel transformation to extents for generic distributed reaction systems that include tubular reactors and reactive separation columns. As a consequence, the well-known concept of extents for batch reactors, which has recently been extended to open homogeneous and heterogeneous reactors [18, 19], as shown in Chapter

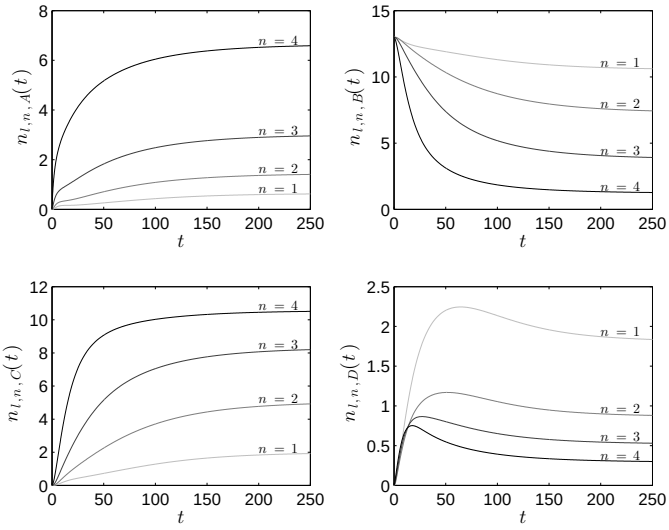

Figure 3.10 – Numbers of moles $\mathbf{n}_{l,n}(t)$ in kmol over time (in minutes) on each of the 4 trays of a reactive distillation column.

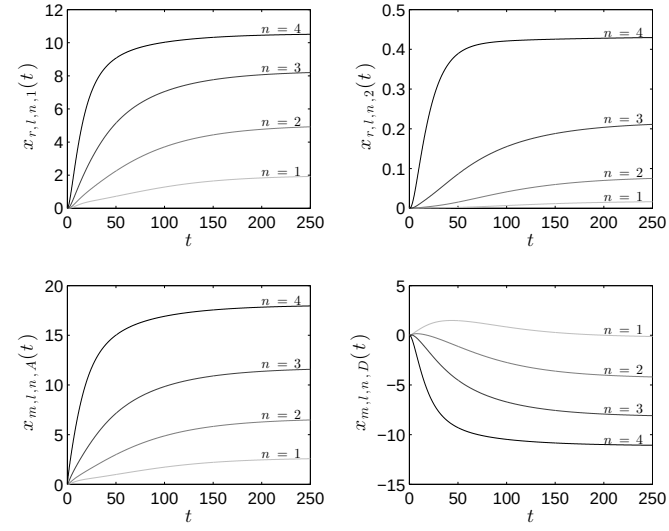

Figure 3.11 – Extents of reaction $\mathbf{x}_{r,l,n}(t)$ and of mass transfer $\mathbf{x}_{m,l,n}(t)$ in kmol over time (in minutes) on each of the 4 trays of a reactive distillation column.

2, has been generalized to distributed reaction systems.

In agreement with the definition of a *vessel extent* for lumped reaction systems, each extent in a distributed reaction system describes uniquely and completely a particular rate process, taking into account the amount that has been transported by advection to a farther position and that has been removed by an outlet. The original concentration variables can always be expressed as the linear transformation of the extents. In many cases, these extents can, in turn, be obtained via the (inverse) linear transformation of the original concentrations. This linear transformation uses structural information about the reaction system, in particular its stoichiometry, the knowledge of the species that transfer between phases and diffuse, as well as information about the initial and boundary conditions. For distributed reaction systems, the initial and boundary conditions replace the initial and inlet conditions required for the transformation of lumped reaction systems. The applicability of these transformations for distributed reaction systems has been demonstrated via simulated examples.

Possible extensions of the concept of extents presented in this chapter include alternative definitions of extents that require less strict rank conditions for the existence of the linear transformation to extents and the connection between extents and analytical or semi-analytical solutions to the PDEs that describe certain distributed reaction systems [91].

The generalization of the concept of extents to distributed reaction systems opens up new perspectives for industrially relevant applications in terms of design, modeling, model identification, model reduction, state reconstruction, data reconciliation, state estimation, monitoring, fault diagnosis, control and optimization of distributed reaction systems. These systems include one- and two-dimensional tubular reactors, three-dimensional reaction systems, micro-reactors, and reactive separation systems, such as reactive absorption or reactive distillation columns. These perspectives for applications of the concept of extents in distributed reaction systems are justified by the fact that some of these applications have been investigated for lumped reaction systems, while others have already been mentioned for the case of distributed reaction systems, namely design, modeling, monitoring and fault diagnosis. For example, the concept of extents has been used for incremental model identification of plug-flow reactors [92].

In summary, a clear understanding of the concept of extents in distributed reaction systems, which has been the main goal of this chapter, will certainly be helpful for the future development of useful applications in chemical engineering.

4 Estimation of Kinetic Parameters via the Incremental Approach

This chapter is adapted from the postprints of the following articles [93, 94]:

D. Rodrigues, J. Billeter, and D. Bonvin. Global identification of kinetic parameters via the extent-based incremental approach. *Comput. Aided Chem. Eng.*, 40:2119–2124, 2017.

Link: http://doi.org/10.1016/B978-0-444-63965-3.50355-X.

D. Rodrigues, J. Billeter, and D. Bonvin. Maximum-likelihood estimation of kinetic parameters via the extent-based incremental approach. *Comput. Chem. Eng.*, in press, 2018.

Link: http://doi.org/10.1016/j.compchemeng.2018.05.024.

The author of this thesis contributed to those articles by developing the main novel ideas, implementing the simulations, and writing a significant part of the text. Hence, the author retains the right to include the articles in this thesis since they are not published commercially and the journal is referenced as the original source.

4.1 Introduction

The identification of reaction kinetics represents one of the main challenges in building first-principles models for reaction systems. Although the literature on this topic is extensive and includes several well-established textbooks [95, 96, 97], there remain significant challenges. This chapter addresses some of these challenges for lumped homogeneous reaction systems. Typically, the identification task consists in confronting a set of candidate rate laws to experimental data and identifying the rate laws and the kinetic parameters that provide the best fit. This identification task can be performed via a simultaneous or an incremental approach as discussed next.

- *Simultaneous identification* is performed by postulating a rate law for each reaction in the model and estimating all kinetic parameters simultaneously. The modeled rates are integrated numerically, and all the parameters are estimated together so as to minimize

the deviations between model predictions and measurements. The procedure is repeated for *all combinations* of rate candidates, and the best combination is selected via appropriate model discrimination techniques. The main advantage of the simultaneous approach is that it leads to statistically optimal parameter estimates in the maximum-likelihood sense. Although these parameter estimates are generally not unbiased, they are consistent in the sense that the estimates converge to the true parameter values as the number of data points tends to infinity [98]. However, simultaneous identification can be computationally costly when there are many combinations of rate candidates to be tested. Moreover, enforcing convergence to global optimality is often slow, difficult and dependent on the initial guesses due to the large number of parameters that need to be estimated simultaneously. Finally, since structural mismatch in one part of the model typically results in errors in all parameters, it is difficult to attribute the mismatch to a particular part of the model.

- *Incremental identification* is performed in several steps by decomposing the identification task into a set of smaller subproblems, with each subproblem corresponding to a single reaction. Hence, since each reaction is investigated individually, only the rate candidates for one reaction at a time need to be compared, and there are fewer parameters to be estimated simultaneously [59]. These parameters are estimated such that the model predictions fit the experimental data of the corresponding reaction. Then, the rate candidate with the best fit is selected.

Note that the estimation of kinetic parameters can be done using either the differential or the integral method. In the *differential method*, the kinetic parameters are estimated by fitting the candidate rate laws to the experimental rates that are generated through differentiation of measured concentrations [99, 60, 61]. In the *integral method*, the kinetic parameters are estimated by fitting the integral of the candidate rate laws to either experimental numbers of moles (with the simultaneous approach) or experimental extents (with the incremental approach) [64].

In the context of the incremental approach, the aforementioned differential and integral methods are also known as rate-based and extent-based approaches. Hence, in extent-based incremental identification, the measured numbers of moles are first transformed to experimental extents via linear transformation as shown in Chapter 2, and then the rate laws are identified individually by comparing the experimental extents to the modeled extents that result from integration of the candidate rate laws. Compared to the rate-based approach, the extent-based incremental approach provides parameter estimates with less bias, tighter confidence intervals and increased ability to discriminate among rate law candidates. However, it also requires more computational effort due to the need to integrate the rates numerically [58].

The main advantage of the incremental methods is that, thanks to the decoupling of the estimation problems, the number of rate candidates can be kept low for each subproblem, and convergence is faster. The main drawback is the fact that the candidate rate laws must be evaluated using measured concentrations because each rate is simulated individually

and there is no information about the other rates. Since the rates that are computed from measured concentrations are typically biased, this bias is propagated to the identification problem, and the parameter estimates are not statistically optimal. Hence, simultaneous identification is typically performed in a final step, using the model structure identified via the incremental approach. This procedure results in statistically optimal parameter estimates and less computational effort than a purely simultaneous approach, because the rate laws are fixed and good initial parameter values are available. An alternative is to use a sequential approach, whereby the rate laws for the various reactions are identified sequentially [100]. This approach shares the advantages of the simultaneous approach, provided that the correct model structure is chosen at each step, while it lies in between the simultaneous and the incremental approaches in terms of computational effort.

A drawback of these kinetic identification approaches is that, since they typically rely on local search methods, they can only converge to locally optimal parameters. This means that, if the solution to the identification problem does not correspond to the global optimum, the identified model may yield an incorrect description of the reaction system. Note that the incremental approach is better suited to global optimization since each estimation subproblem involves a small number of parameters. Taking these considerations into account, an incremental parameter estimation method has been proposed to obtain globally optimal parameter estimates [101]. However, this estimation method is based on (i) the rate-based incremental approach, which can have several disadvantages compared to the extent-based approach as mentioned above, and (ii) branch-and-bound techniques, which are known to exhibit a worst-case complexity that is exponential in the number of decision variables.

This chapter presents a novel methodology for the identification of kinetic parameters for lumped homogeneous reaction systems. The novelty consists in (i) adopting the extent-based incremental approach, (ii) leading to statistically optimal parameter estimates in the maximum-likelihood sense, and (iii) guaranteeing convergence to global optimality. The global solution to this incremental approach has a quality similar to the global solution to the simultaneous approach but with a much smaller computational effort. The proposed approach does not rely on branch-and-bound techniques but rather on the reformulation of the nonconvex optimization problem as a convex problem, thereby taking advantage of the developments in polynomial optimization using sum-of-squares polynomials and semidefinite programming [102].

The structure of the chapter is as follows. Section 4.2 reviews the concept of extents as well as the procedure for model identification using the extent-based incremental approach. Section 4.3 presents two important steps necessary to guarantee maximum-likelihood parameter estimates with the extent-based incremental approach. Section 4.4 discusses the reformulation of the original identification problem as a convex optimization problem and its solution. A simulated case study is presented in Section 4.5, while Section 4.6 concludes the chapter.

4.2 Extent-based Incremental Approach

This section reviews the fundamental features of extent-based incremental model identification. In incremental identification, each reaction is dealt with individually. Consequently, for each reaction, only the rate candidates for that reaction need to be compared, which requires estimating only the parameters of a given candidate at a time.

4.2.1 Concept of vessel extents

The concept of vessel extents is instrumental for the application of the extent-based incremental approach to model identification. This concept is briefly described next.

Let us consider an open lumped homogeneous reactor with S species involved in R independent reactions, p independent inlets and one outlet. The state of the reactor is typically represented by the volume $V(t)$, the S-dimensional vector of concentrations $\mathbf{c}(t)$ and the temperature $T(t)$. Upon defining the numbers of moles $\mathbf{n}(t) := V(t)\,\mathbf{c}(t)$, one can write the mole balance equations as

$$\dot{\mathbf{n}}(t) = \mathbf{N}^{\mathrm{T}}\, V(t)\,\mathbf{r}(t) + \mathbf{W}_{in}\,\mathbf{u}_{in}(t) - \omega(t)\,\mathbf{n}(t), \qquad \mathbf{n}(0) = \mathbf{n}_0, \tag{4.1}$$

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

The concept of vessel extents can also be used to represent the system dynamics [18]. The i^{th} vessel extent of reaction, which represents the amount of material that has been processed by the i^{th} reaction and is in the vessel at time t, is described by the differential equation

$$\dot{x}_{r,i}(t) = V(t)\, r_i(t) - \omega(t) x_{r,i}(t), \qquad x_{r,i}(0) = 0, \qquad i = 1, \ldots, R. \tag{4.2}$$

The j^{th} vessel extent of inlet, which represents the amount of material that has flowed into the reactor via the j^{th} inlet and is in the vessel at time t, is described by

$$\dot{x}_{in,j}(t) = u_{in,j}(t) - \omega(t) x_{in,j}(t), \qquad x_{in,j}(0) = 0, \qquad j = 1, \ldots, p. \tag{4.3}$$

The vessel extent of initial conditions, which represents the amount of material that was initially in the reactor and is in the vessel at time t, is described by

$$\dot{x}_{ic}(t) = -\omega(t) x_{ic}(t), \qquad x_{ic}(0) = 1. \tag{4.4}$$

Consequently, upon considering the reaction rates and inlet flowrates as (endogenous

and exogenous) inputs, the extents can be written as convolution integrals. The i^{th} vessel extent of reaction is

$$x_{r,i}(t) = \int_0^t V(\tau)\, r_i(\tau)\, e^{-\int_\tau^t \omega(\zeta)\mathrm{d}\zeta}\mathrm{d}\tau, \qquad i = 1,\ldots,R, \tag{4.5}$$

the j^{th} vessel extent of inlet is

$$x_{in,j}(t) = \int_0^t u_{in,j}(\tau)\, e^{-\int_\tau^t \omega(\zeta)\mathrm{d}\zeta}\mathrm{d}\tau, \qquad j = 1,\ldots,p, \tag{4.6}$$

and the vessel extent of initial conditions is

$$x_{ic}(t) = e^{-\int_0^t \omega(\zeta)\mathrm{d}\zeta}. \tag{4.7}$$

Moreover, the numbers of moles are given by the linear combinations of extents

$$\mathbf{n}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{x}_r(t) + \mathbf{W}_{in}\mathbf{x}_{in}(t) + \mathbf{n}_0\, x_{ic}(t), \tag{4.8}$$

where the p-dimensional vector of extents of inlet $\mathbf{x}_{in}$ and the extent of initial conditions x_{ic} can be computed from the knowledge of inlet and outlet flowrates, as shown in Section 2.5.

Then, provided that $\mathrm{rank}\,(\mathbf{N}) = R$, it is possible to compute $\tilde{\mathbf{x}}_r$ from the measurements $\tilde{\mathbf{c}}$ as

$$\tilde{\mathbf{x}}_r(t) = \left(\mathbf{N}\boldsymbol{\Sigma}_{\tilde{\mathbf{c}}}^{-1}\mathbf{N}^{\mathrm{T}}\right)^{-1}\mathbf{N}\boldsymbol{\Sigma}_{\tilde{\mathbf{c}}}^{-1}\left(V(t)\,\tilde{\mathbf{c}}(t) - \mathbf{W}_{in}\mathbf{x}_{in}(t) - \mathbf{n}_0 x_{ic}(t)\right), \tag{4.9}$$

where $\tilde{(\cdot)}$ denotes noisy quantities and $\boldsymbol{\Sigma}_{\tilde{\mathbf{c}}}$ is the variance-covariance matrix of $\tilde{\mathbf{c}}$.

Although the extent-based incremental approach is detailed here only for open lumped homogeneous reactors, this approach can also be used for many other types of reaction systems. Indeed, the concept of extents described in Eqs. (4.2)–(4.8) is rather general and can be extended to heterogeneous reactors with mass transfer, reactors with heat balance, reactors with instantaneous equilibria described by differential-algebraic equations as well as tubular reactors and reactive separation columns described by partial differential equations, as shown in Chapters 2 and 3. Moreover, the expression of the extents as convolution integrals presented in Eqs. (4.5)–(4.7) is also general and can even be demonstrated for tubular reactors with reaction, advection, and diffusion [91].

4.2.2 Rate laws

The incremental approach deals with one rate candidate at a time. The rate candidates for a given reaction correspond to plausible rate laws, with each decision variable being an unknown kinetic parameter that belongs to an interval of real numbers.

Let us assume that each rate law is (i) a function of $\mathbf{z}(t) := \left[\mathbf{c}(t)^{\mathrm{T}} \;\; T(t)\right]^{\mathrm{T}}$, and (ii)

linear in the L parameters $\boldsymbol{\alpha} = (\alpha_1, \ldots, \alpha_L)$ and nonlinear in the N parameters $\boldsymbol{\theta} = (\theta_1, \ldots, \theta_N)$. Hence, we propose to express the reaction rate as

$$r\big(\mathbf{z}(t), \boldsymbol{\alpha}, \boldsymbol{\theta}\big) = r_0\big(\mathbf{z}(t), \boldsymbol{\theta}\big) + \sum_{\ell=1}^{L} \alpha_\ell \, r_\ell\big(\mathbf{z}(t), \boldsymbol{\theta}\big). \tag{4.10}$$

The goal is to estimate the kinetic parameters $\boldsymbol{\alpha}$ and $\boldsymbol{\theta}$ from measurements.

4.2.3 Identification problem

Considering the generic rate candidate $r\big(\mathbf{z}(t), \boldsymbol{\alpha}, \boldsymbol{\theta}\big)$, the corresponding vessel extent of reaction is

$$\begin{aligned} x_r(t, \boldsymbol{\alpha}, \boldsymbol{\theta}) &= \int_0^t V(\tau)\, r\big(\mathbf{z}(\tau), \boldsymbol{\alpha}, \boldsymbol{\theta}\big)\, e^{-\int_\tau^t \omega(\zeta)\mathrm{d}\zeta} \mathrm{d}\tau \\ &= V(t)\, d_0(t, \boldsymbol{\theta}) + \sum_{\ell=1}^{L} \alpha_\ell V(t)\, d_\ell(t, \boldsymbol{\theta}), \end{aligned} \tag{4.11}$$

where

$$\begin{aligned} d_\ell(t, \boldsymbol{\theta}) &:= \int_0^t \tfrac{V(\tau)}{V(t)}\, r_\ell\big(\mathbf{z}(\tau), \boldsymbol{\theta}\big)\, e^{-\int_\tau^t \omega(\zeta)\mathrm{d}\zeta} \mathrm{d}\tau \\ &= \int_0^t r_\ell\big(\mathbf{z}(\tau), \boldsymbol{\theta}\big) \tfrac{x_{ic}(t)/V(t)}{x_{ic}(\tau)/V(\tau)} \mathrm{d}\tau, \qquad \forall \ell = 0, \ldots, L. \end{aligned} \tag{4.12}$$

In practice, the noisy measurements $\tilde{\mathbf{z}}$ are available with the sampling period h at the time instants $t_m := mh$, for $m = 0, \ldots, H$. Upon numerical integration via a quadrature method specified by weights γ_m (for example, Simpson's rule) and replacing $r_\ell\big(\mathbf{z}(t_m), \boldsymbol{\theta}\big)$ by its estimate $\hat{r}_\ell\big(\tilde{\mathbf{z}}(t_m), \boldsymbol{\theta}\big)$, $d_\ell(t, \boldsymbol{\theta})$ is approximated by

$$\hat{d}_\ell(t, \boldsymbol{\theta}) := \sum_{m=0}^{\frac{t}{h}} h\gamma_m \hat{r}_\ell\big(\tilde{\mathbf{z}}(t_m), \boldsymbol{\theta}\big) \tfrac{x_{ic}(t)/V(t)}{x_{ic}(t_m)/V(t_m)}, \qquad \forall \ell = 0, \ldots, L. \tag{4.13}$$

Remark 4.1. Note that the approximation of $d_\ell(t, \boldsymbol{\theta})$ by $\hat{d}_\ell(t, \boldsymbol{\theta})$ entails two different types of errors, which occur because only noisy measurements at discrete time instants $\tilde{\mathbf{z}}(t_m)$ are available:

1. Propagation error (PE): This error is due to the propagation of noise in the measurements to the modeled rate $\hat{r}_\ell\big(\tilde{\mathbf{z}}(t_m), \boldsymbol{\theta}\big)$. Hence, the propagation error accounts for the difference between the cases of noisy measurements $\tilde{\mathbf{z}}(t_m)$ and noise-free measure-

ments $\mathbf{z}(t_m)$. It is defined as:

$$\mathrm{PE}_\ell(t,\boldsymbol{\theta}) := \sum_{m=0}^{\frac{t}{h}} h\gamma_m \Big(\hat{r}_\ell\big(\tilde{\mathbf{z}}(t_m),\boldsymbol{\theta}\big) - r_\ell\big(\mathbf{z}(t_m),\boldsymbol{\theta}\big) \Big) \tfrac{x_{ic}(t)/V(t)}{x_{ic}(t_m)/V(t_m)}, \quad \forall \ell = 0,\dots,L. \tag{4.14}$$

2. Integration error (IE): This error is due to the use of numerical integration that is needed because the measurements are available only at discrete time instants. Hence, the integration error would also occur if noise-free measurements $\mathbf{z}(t_m)$ were available. It is defined as:

$$\begin{aligned}\mathrm{IE}_\ell(t,\boldsymbol{\theta}) := &\sum_{m=0}^{\frac{t}{h}} h\gamma_m r_\ell\big(\mathbf{z}(t_m),\boldsymbol{\theta}\big) \tfrac{x_{ic}(t)/V(t)}{x_{ic}(t_m)/V(t_m)} \\ &- \int_0^t r_\ell\big(\mathbf{z}(\tau),\boldsymbol{\theta}\big) \tfrac{x_{ic}(t)/V(t)}{x_{ic}(\tau)/V(\tau)} \mathrm{d}\tau, \quad \forall \ell = 0,\dots,L. \end{aligned} \tag{4.15}$$

It follows from the definitions of the propagation and integration errors in Remark 4.1 that:

$$\hat{d}_\ell(t,\boldsymbol{\theta}) - d_\ell(t,\boldsymbol{\theta}) = \mathrm{PE}_\ell(t,\boldsymbol{\theta}) + \mathrm{IE}_\ell(t,\boldsymbol{\theta}), \qquad \forall \ell = 0,\dots,L. \tag{4.16}$$

If r is a rate candidate for the i^{th} reaction, the identification problem of the extent-based incremental approach for this rate candidate reads:

$$\min_{\boldsymbol{\alpha},\boldsymbol{\theta}} J(\boldsymbol{\alpha},\boldsymbol{\theta}) = \sum_{m=1}^{H} \left(\frac{\hat{x}_r(t_m,\boldsymbol{\alpha},\boldsymbol{\theta}) - \tilde{x}_{r,i}(t_m)}{V(t_m)} \right)^2, \tag{4.17}$$

with the modeled extent

$$\hat{x}_r(t_m,\boldsymbol{\alpha},\boldsymbol{\theta}) := V(t_m)\hat{d}_0(t_m,\boldsymbol{\theta}) + \sum_{\ell=1}^{L} \alpha_\ell V(t_m)\hat{d}_\ell(t_m,\boldsymbol{\theta}) \tag{4.18}$$

linear in $\boldsymbol{\alpha}$, and the experimental extents $\tilde{\mathbf{x}}_r(t_m)$ expressed as the linear transformation of the concentrations $\tilde{\mathbf{c}}(t_m)$ in Eq. (4.9).

Remark 4.2. The formulation of the identification problem in Eq. (4.17) assumes that each element of $\tilde{\mathbf{c}}$ is corrupted by independent and identically distributed (i.i.d.) noise with respect to time, that is, the noise in $\tilde{\mathbf{c}}$ is homoscedastic. In this case, one can infer from Eq. (4.9) that each term $\frac{\tilde{x}_{r,i}}{V}$ is also corrupted by homoscedastic noise, whereas the noise in $\tilde{x}_{r,i}$ is heteroscedastic. For this reason, the cost of the identification problem consists in the sum of squares of differences between the modeled quantity $\frac{\hat{x}_r}{V}$ and the corresponding experimental quantity $\frac{\tilde{x}_{r,i}}{V}$ rather than between $\hat{x}_r$ and $\tilde{x}_{r,i}$.

4.2.4 Reformulation of the identification problem

The cost function in Eq. (4.17) is quadratic in $\boldsymbol{\alpha}$, that is,

$$J(\boldsymbol{\alpha},\boldsymbol{\theta}) = c(\boldsymbol{\theta}) + 2\boldsymbol{\alpha}^{\mathrm{T}}\mathbf{g}(\boldsymbol{\theta}) + \boldsymbol{\alpha}^{\mathrm{T}}\mathbf{H}(\boldsymbol{\theta})\boldsymbol{\alpha}, \tag{4.19}$$

with

$$c(\boldsymbol{\theta}) := \sum_{m=1}^{H}\left(\hat{d}_0(t_m,\boldsymbol{\theta}) - \frac{\tilde{x}_{r,i}(t_m)}{V(t_m)}\right)^2, \tag{4.20a}$$

$$\mathbf{g}(\boldsymbol{\theta}) := \sum_{m=1}^{H}\hat{\mathbf{d}}(t_m,\boldsymbol{\theta})\left(\hat{d}_0(t_m,\boldsymbol{\theta}) - \frac{\tilde{x}_{r,i}(t_m)}{V(t_m)}\right), \tag{4.20b}$$

$$\mathbf{H}(\boldsymbol{\theta}) := \sum_{m=1}^{H}\hat{\mathbf{d}}(t_m,\boldsymbol{\theta})\hat{\mathbf{d}}(t_m,\boldsymbol{\theta})^{\mathrm{T}}, \tag{4.20c}$$

where $\hat{\mathbf{d}}(t_m,\boldsymbol{\theta}) := \begin{bmatrix}\hat{d}_1(t_m,\boldsymbol{\theta}) & \cdots & \hat{d}_L(t_m,\boldsymbol{\theta})\end{bmatrix}^{\mathrm{T}}$. Note that $\mathbf{H}(\boldsymbol{\theta})$ is invertible since $\mathbf{H}(\boldsymbol{\theta}) \succ \mathbf{0}_{L\times L}$.

The optimal parameters $\boldsymbol{\alpha}$ can be computed for each $\boldsymbol{\theta}$ as

$$\hat{\boldsymbol{\alpha}}(\boldsymbol{\theta}) = -\mathbf{H}(\boldsymbol{\theta})^{-1}\mathbf{g}(\boldsymbol{\theta}), \tag{4.21}$$

which allows an exact reformulation of the optimization problem described in Eq. (4.17) with only the decision variables $\boldsymbol{\theta}$:

$$\min_{\boldsymbol{\theta}} \bar{J}(\boldsymbol{\theta}) = J\left(\hat{\boldsymbol{\alpha}}(\boldsymbol{\theta}),\boldsymbol{\theta}\right) = c(\boldsymbol{\theta}) - \mathbf{g}(\boldsymbol{\theta})^{\mathrm{T}}\mathbf{H}(\boldsymbol{\theta})^{-1}\mathbf{g}(\boldsymbol{\theta}). \tag{4.22}$$

One can also compute

$$\frac{\partial \bar{J}}{\partial \theta_k}(\boldsymbol{\theta}) = \frac{\partial c}{\partial \theta_k}(\boldsymbol{\theta}) + 2\hat{\boldsymbol{\alpha}}(\boldsymbol{\theta})^{\mathrm{T}}\frac{\partial \mathbf{g}}{\partial \theta_k}(\boldsymbol{\theta}) + \hat{\boldsymbol{\alpha}}(\boldsymbol{\theta})^{\mathrm{T}}\frac{\partial \mathbf{H}}{\partial \theta_k}(\boldsymbol{\theta})\hat{\boldsymbol{\alpha}}(\boldsymbol{\theta}), \qquad \forall k = 1,\ldots,N, \tag{4.23}$$

analytically to speed up convergence of the optimization algorithm to a local minimum.

Remark 4.3. A similar separation of parameters has been proposed for the simultaneous approach to avoid having to determine more parameters via optimization when the initial conditions are unknown or rate measurements are considered [103]. However, it is assumed here that the initial conditions are known and no rate measurements are considered. Hence, it is not possible to separate any of the parameters with the simultaneous approach since the modeled numbers of moles $\hat{\mathbf{n}}(t_m,\boldsymbol{\alpha},\boldsymbol{\theta})$ depend nonlinearly on all the parameters $\boldsymbol{\alpha}$ and $\boldsymbol{\theta}$. This is due to the fact that, in the simultaneous approach, the modeled numbers of moles result from the numerical integration of rates that are computed from *modeled* quantities at arbitrary time instants $\hat{\mathbf{z}}(t,\boldsymbol{\alpha},\boldsymbol{\theta})$. In contrast, in the incremental approach, the rates are

computed from *measured* quantities at discrete time instants $\tilde{\mathbf{z}}(t_m)$, which explains why the modeled extent $\hat{x}_r(t_m, \boldsymbol{\alpha}, \boldsymbol{\theta})$ is linear in $\boldsymbol{\alpha}$.

Remark 4.4. The incremental approach does not provide statistically optimal parameters in the maximum-likelihood sense for two main reasons: (i) if the experimental extents $\tilde{x}_{r,1}, \ldots, \tilde{x}_{r,R}$ are correlated, this correlation is not taken into account by solving the identification problem individually for each reaction; (ii) if the estimate of $r_\ell\left(\mathbf{z}(t_m), \boldsymbol{\theta}\right)$ computed from the measurements $\tilde{\mathbf{z}}(t_m)$ is biased, the numerical integration of these biased estimates results in a biased value $\hat{d}_\ell(t_m, \boldsymbol{\theta})$, which implies that the modeled extent $\hat{x}_r(t_m, \boldsymbol{\alpha}, \boldsymbol{\theta})$ is also biased. The next section suggests methods to deal with these two issues. Note that the propagation and integration errors mentioned in Remark 4.1 will always be present with the incremental approach. However, these errors can be kept rather small provided that the sampling is sufficiently frequent and the propagation error is unbiased.

4.3 Maximum-likelihood Estimation via the Extent-based Incremental Approach

This section introduces a new feature of extent-based incremental model identification, namely, the fact that this approach can be used to obtain maximum-likelihood parameter estimates. For this, two methods are developed next: (i) a method to compute *uncorrelated experimental extents*, which allows solving the identification problem individually for each reaction without neglecting the correlation between the various experimental extents; and (ii) a method to compute rate estimates with negligible bias, which results in *modeled extents with negligible bias* and contributes to reduce the bias in the parameter estimates.

4.3.1 Computation of uncorrelated experimental extents

This subsection shows how one can compute uncorrelated experimental extents from a set of measurements that depend linearly on these extents. Since the incremental approach requires the knowledge of the relationship between extents and measured quantities, the relationship between numbers of moles (or concentrations) and measured quantities needs to be known. Hence, before discussing the computation of the experimental extents $\tilde{\mathbf{x}}_r$ from the noisy measurements $\tilde{\mathbf{y}}$, let us investigate the computation of the experimental concentrations $\tilde{\mathbf{c}}$ from $\tilde{\mathbf{y}}$ via calibration. For the sake of simplicity, the time dependence is omitted in the remainder of this subsection.

4.3.1.1 Computation of experimental concentrations from $\tilde{\mathbf{y}}$ via calibration

Let us denote the W-dimensional vector of measured quantities as $\mathbf{y}$, the corresponding vector of noisy measurements as $\tilde{\mathbf{y}}$, and the $S \times W$ matrix of molar sensitivities as $\mathbf{S}$.

Assuming the measurement model

$$\mathbf{y} = \mathbf{S}^{\mathrm{T}}\mathbf{c}, \tag{4.24}$$

$\tilde{\mathbf{c}}$ can be computed from $\tilde{\mathbf{y}}$ using an equation of the form

$$\tilde{\mathbf{c}} = \mathbf{V}_{pr}\tilde{\mathbf{y}}, \tag{4.25}$$

where the prognostic matrix $\mathbf{V}_{pr}$ is any matrix that satisfies

$$\mathbf{V}_{pr}\mathbf{S}^{\mathrm{T}} = \mathbf{I}_S. \tag{4.26}$$

The matrix $\mathbf{S}$ can be computed via calibration using H experiments that yield the $H \times W$ matrix of calibration measurements $\mathbf{Y}_{cal}$ and the $H \times S$ matrix of calibration concentrations $\mathbf{C}_{cal}$ of rank S:

$$\mathbf{S} = \mathbf{C}_{cal}^{+}\mathbf{Y}_{cal}, \tag{4.27}$$

where $\mathbf{C}_{cal}^{+} := \left(\mathbf{C}_{cal}^{\mathrm{T}}\mathbf{C}_{cal}\right)^{-1}\mathbf{C}_{cal}^{\mathrm{T}}$ is the Moore-Penrose pseudoinverse of $\mathbf{C}_{cal}$.

The prognostic matrix $\mathbf{V}_{pr}$ can be computed from $\mathbf{S}$ in Eq. (4.27) in different ways. For example:

- Provided that $\mathrm{rank}(\mathbf{S}) = S$, one can use $\mathbf{S}$ to compute $\tilde{\mathbf{c}}$ from $\tilde{\mathbf{y}}$ as

  $$\tilde{\mathbf{c}} = \left(\mathbf{S}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}}^{-1}\mathbf{S}^{\mathrm{T}}\right)^{-1}\mathbf{S}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}}^{-1}\tilde{\mathbf{y}}, \tag{4.28}$$

  where $\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}}$ is the variance-covariance matrix of $\tilde{\mathbf{y}}$. Then, the variance-covariance matrix of $\tilde{\mathbf{c}}$ is

  $$\boldsymbol{\Sigma}_{\tilde{\mathbf{c}}} = \left(\mathbf{S}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}}^{-1}\mathbf{S}^{\mathrm{T}}\right)^{-1}. \tag{4.29}$$

  Replacing $\mathbf{S}$ in Eq. (4.28) corresponds to a particular choice of $\mathbf{V}_{pr}$, that is,

  $$\mathbf{V}_{pr} = \mathbf{C}_{cal}^{\mathrm{T}}\mathbf{C}_{cal}\left(\mathbf{C}_{cal}^{\mathrm{T}}\mathbf{Y}_{cal}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}}^{-1}\mathbf{Y}_{cal}^{\mathrm{T}}\mathbf{C}_{cal}\right)^{-1}\mathbf{C}_{cal}^{\mathrm{T}}\mathbf{Y}_{cal}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}}^{-1}. \tag{4.30}$$

- Another particular choice that also satisfies Eq. (4.26) and uses $\mathbf{S}$ from Eq. (4.27) is

  $$\mathbf{V}_{pr} = \mathbf{C}_{cal}^{\mathrm{T}}\left(\mathbf{Y}_{cal}^{\mathrm{T}}\right)^{+}, \tag{4.31}$$

  which corresponds to principal component regression (PCR), if one considers $\mathbf{Y}_{cal}$ as the result of a singular value decomposition with a reduced number of singular values [104].

4.3.1.2 Computation of experimental extents from $\tilde{\mathbf{y}}$

From Eqs. (4.8) and (4.24), one can write the re-arranged measurement model as

$$V\mathbf{y} = \mathbf{S}^{\mathrm{T}}\left(\mathbf{N}^{\mathrm{T}}\mathbf{x}_r + \mathbf{W}_{in}\mathbf{x}_{in} + \mathbf{n}_0 x_{ic}\right). \tag{4.32}$$

Provided that $\mathrm{rank}(\mathbf{N}) = R$ and $\mathrm{rank}(\mathbf{S}) = S$, it is possible to relate $\tilde{\mathbf{x}}_r$ to $\tilde{\mathbf{c}}$ using Eq. (4.9) and to $\tilde{\mathbf{y}}$ using Eqs. (4.28) and (4.29):

$$\tilde{\mathbf{x}}_r = \left(\mathbf{N}\mathbf{S}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}}^{-1}\mathbf{S}^{\mathrm{T}}\mathbf{N}^{\mathrm{T}}\right)^{-1}\mathbf{N}\mathbf{S}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}}^{-1}\left(V\tilde{\mathbf{y}} - \mathbf{S}^{\mathrm{T}}\left(\mathbf{W}_{in}\mathbf{x}_{in} + \mathbf{n}_0 x_{ic}\right)\right). \tag{4.33}$$

Eq. (4.33) can also be obtained directly from Eq. (4.32) if the less restrictive condition $\mathrm{rank}(\mathbf{N}\mathbf{S}) = R$ is satisfied.

Remark 4.5. A consequence of Eq. (4.33) is that the experimental extents $\tilde{\mathbf{x}}_r$ are typically correlated, even if the measurements $\tilde{\mathbf{y}}$ are uncorrelated.

4.3.1.3 Computation of uncorrelated experimental extents from $\tilde{\mathbf{y}}$

The goal is to use the measurements $\tilde{\mathbf{y}}$ in a way that allows obtaining *uncorrelated* experimental extents $\tilde{x}_{r,1}, \ldots, \tilde{x}_{r,R}$. Assuming that the measurements $\tilde{\mathbf{y}}$ are uncorrelated, a simple way of generating uncorrelated experimental extents is to compute the various extents from different measurements $\tilde{\mathbf{y}}$, which can be written as

$$\begin{cases} \tilde{x}_{r,i} = \sum_{w=1}^{W} c_{i,w}\tilde{y}_w \\ \tilde{x}_{r,j} = \sum_{w=1}^{W} c_{j,w}\tilde{y}_w \end{cases} \Rightarrow i = j \vee c_{i,w} = 0 \vee c_{j,w} = 0, \quad \forall w = 1, \ldots, W. \tag{4.34}$$

In other words, one determines a partition $\tilde{\mathbf{y}}_1, \ldots, \tilde{\mathbf{y}}_R$ of $\tilde{\mathbf{y}}$ and computes each $\tilde{x}_{r,i}$ from the corresponding $\tilde{\mathbf{y}}_i$, for all $i = 1, \ldots, R$.

Remark 4.6. Section 4.3.1 is built upon the assumptions of (i) a linear relationship between the measured quantities $\mathbf{y}$ and the concentrations $\mathbf{c}$, and (ii) the availability of uncorrelated measurements $\tilde{\mathbf{y}}$. Alternatively, if these assumptions are not satisfied, the methodology can still be adapted to generate uncorrelated experimental extents $\tilde{x}_{r,1}, \ldots, \tilde{x}_{r,R}$ from the measurements $\tilde{\mathbf{y}}$ (this is not discussed any further here). Note that, in the particular case of kinetic modeling using spectroscopic measurements, it is typically assumed that (i) the Beer-Lambert law is valid, which implies there exists a linear relationship between the measured quantities $\mathbf{y}$ (absorbances) and the concentrations $\mathbf{c}$, and (ii) the different measurements $\tilde{\mathbf{y}}$ at different wavelengths are uncorrelated [105]. However, the methodology in this section is more general and not limited to spectroscopic measurements.

Consider the W_i-dimensional subset of measured quantities, $\mathbf{y}_i$, with the corresponding

$S \times W_i$ submatrix of molar sensitivities $\mathbf{S}_i$. Then, Eq. (4.32) can be written as

$$V\mathbf{y}_i = \mathbf{S}_i^{\mathrm{T}} \left(\mathbf{N}^{\mathrm{T}} \mathbf{x}_r + \mathbf{W}_{in} \mathbf{x}_{in} + \mathbf{n}_0 x_{ic} \right). \tag{4.35}$$

Let us assume that $\mathbf{y}_i$ is affected by only R_i reactions, with the corresponding extents of reaction $\mathbf{x}_{r,i}$ and the $R_i \times S$ stoichiometric submatrix $\mathbf{N}_i$, which allows writing:

$$V\mathbf{y}_i = \mathbf{S}_i^{\mathrm{T}} \left(\mathbf{N}_i^{\mathrm{T}} \mathbf{x}_{r,i} + \mathbf{W}_{in} \mathbf{x}_{in} + \mathbf{n}_0 x_{ic} \right). \tag{4.36}$$

Provided that rank $(\mathbf{N}_i \mathbf{S}_i) = R_i$, $\tilde{\mathbf{x}}_{r,i}$ can be computed from $\tilde{\mathbf{y}}_i$ as:

$$\tilde{\mathbf{x}}_{r,i} = \mathscr{T}_{r,i} \Big(V\tilde{\mathbf{y}}_i - \mathbf{S}_i^{\mathrm{T}} \left(\mathbf{W}_{in} \mathbf{x}_{in} + \mathbf{n}_0 x_{ic} \right) \Big), \tag{4.37}$$

where $\mathscr{T}_{r,i} := \left(\mathbf{N}_i \mathbf{S}_i \boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}^{-1} \mathbf{S}_i^{\mathrm{T}} \mathbf{N}_i^{\mathrm{T}} \right)^{-1} \mathbf{N}_i \mathbf{S}_i \boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}^{-1}$ and $\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}$ is the variance-covariance matrix of $\tilde{\mathbf{y}}_i$.

This implies that the experimental extent $\tilde{x}_{r,i}$ can be expressed as the linear transformation of the measurements

$$\tilde{x}_{r,i} = \mathbf{t}_{r,i}^{*\mathrm{T}} \Big(V\tilde{\mathbf{y}}_i - \mathbf{S}_i^{\mathrm{T}} \left(\mathbf{W}_{in} \mathbf{x}_{in} + \mathbf{n}_0 x_{ic} \right) \Big), \tag{4.38}$$

where $\mathbf{t}_{r,i}^* := \mathscr{T}_{r,i}^{\mathrm{T}} \mathbf{e}_i$, with $\mathbf{e}_i$ the R_i-dimensional unit vector of the standard basis (that is, a vector with one element equal to 1 and all the other elements equal to 0) that selects the extent of reaction $x_{r,i}$ out of $\mathbf{x}_{r,i}$. Note that $\mathbf{t}_{r,i}^*$ is the solution to the optimization problem

$$\min_{\mathbf{t}_{r,i}} \quad \sigma_{\tilde{x}_{r,i}}^2(\mathbf{t}_{r,i}) = \mathbf{t}_{r,i}^{\mathrm{T}} \boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i} \mathbf{t}_{r,i} \tag{4.39a}$$

$$\text{s.t.} \quad \mathbf{N}_i \mathbf{S}_i \mathbf{t}_{r,i} = \mathbf{e}_i, \tag{4.39b}$$

which enforces minimal variance of $\tilde{x}_{r,i}$, as shown in Appendix C.1. The equality constraint in Eq. (4.39b) ensures that the result is correct in the noise-free case, that is,

$$\mathbf{t}_{r,i}^{\mathrm{T}} \Big(V\mathbf{y}_i - \mathbf{S}_i^{\mathrm{T}} \left(\mathbf{W}_{in} \mathbf{x}_{in} + \mathbf{n}_0 x_{ic} \right) \Big) = \mathbf{t}_{r,i}^{\mathrm{T}} \mathbf{S}_i^{\mathrm{T}} \mathbf{N}_i^{\mathrm{T}} \mathbf{x}_{r,i} = \mathbf{e}_i^{\mathrm{T}} \mathbf{x}_{r,i} = x_{r,i}. \tag{4.40}$$

If one can construct a partition $\tilde{\mathbf{y}}_1, \ldots, \tilde{\mathbf{y}}_R$ of $\tilde{\mathbf{y}}$ and the corresponding partition $\mathbf{S}_1, \ldots, \mathbf{S}_R$ of $\mathbf{S}$ such that, for each $i = 1, \ldots, R$, (i) the matrix $\mathbf{S}_i^{\mathrm{T}} \mathbf{N}_i^{\mathrm{T}}$ that corresponds to the nonzero columns of $\mathbf{S}_i^{\mathrm{T}} \mathbf{N}^{\mathrm{T}}$ has full column rank, and (ii) the extents of reaction $\mathbf{x}_{r,i}$ that correspond to the nonzero columns of $\mathbf{S}_i^{\mathrm{T}} \mathbf{N}^{\mathrm{T}}$ include the extent $x_{r,i}$, then the experimental extents $\tilde{x}_{r,1}, \ldots, \tilde{x}_{r,R}$ computed from the uncorrelated measurements $\tilde{\mathbf{y}}$ will be uncorrelated. This is illustrated in the next example.

4.3.1.4 Example

Let us consider a semi-batch reactor (which implies that $x_{ic} = 1$) with the reactions A + B → C and 2B → D. The reactor is fed with species B. The stoichiometric matrix is

$$\mathbf{N} = \begin{bmatrix} \mathbf{n}_1^{\mathrm{T}} \\ \mathbf{n}_2^{\mathrm{T}} \end{bmatrix} = \begin{bmatrix} -1 & -1 & 1 & 0 \\ 0 & -2 & 0 & 1 \end{bmatrix}. \tag{4.41}$$

Let us assume that there are $W = 3$ uncorrelated measurements of equal variance and the matrix $\mathbf{S}$ has been calibrated as follows:

$$\mathbf{S} = \begin{bmatrix} \mathbf{s}_1 & \mathbf{s}_2 & \mathbf{s}_3 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 3 & 5 \\ 2 & 4 & 0 \\ 0 & 0 & 6 \end{bmatrix}. \tag{4.42}$$

The measurement model in Eq. (4.32) reads:

$$V \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 1 & -6 \\ -5 & -4 \end{bmatrix} \begin{bmatrix} x_{r,1} \\ x_{r,2} \end{bmatrix} + \begin{bmatrix} \mathbf{s}_1^{\mathrm{T}} \\ \mathbf{s}_2^{\mathrm{T}} \\ \mathbf{s}_3^{\mathrm{T}} \end{bmatrix} \left(\mathbf{W}_{in} \mathbf{x}_{in} + \mathbf{n}_0 \right). \tag{4.43}$$

The matrix $\mathbf{S}^{\mathrm{T}}\mathbf{N}^{\mathrm{T}} = \begin{bmatrix} 1 & 0 \\ 1 & -6 \\ -5 & -4 \end{bmatrix}$ suggests selecting

$$\mathbf{y}_1 = \begin{bmatrix} y_1 \end{bmatrix}^{\mathrm{T}}, \qquad \mathbf{S}_1 = \begin{bmatrix} \mathbf{s}_1 \end{bmatrix}, \tag{4.44a}$$

$$\mathbf{y}_2 = \begin{bmatrix} y_2 & y_3 \end{bmatrix}^{\mathrm{T}}, \qquad \mathbf{S}_2 = \begin{bmatrix} \mathbf{s}_2 & \mathbf{s}_3 \end{bmatrix}, \tag{4.44b}$$

with which Eq. (4.36) is satisfied with

$$\mathbf{N}_1^{\mathrm{T}} = \begin{bmatrix} \mathbf{n}_1 \end{bmatrix}, \qquad \mathbf{x}_{r,1} = \begin{bmatrix} x_{r,1} \end{bmatrix}^{\mathrm{T}}, \qquad \operatorname{rank}\left(\mathbf{N}_1 \mathbf{S}_1\right) = \operatorname{rank}(1) = 1, \tag{4.45a}$$

$$\mathbf{N}_2^{\mathrm{T}} = \begin{bmatrix} \mathbf{n}_1 & \mathbf{n}_2 \end{bmatrix}, \quad \mathbf{x}_{r,2} = \begin{bmatrix} x_{r,1} & x_{r,2} \end{bmatrix}^{\mathrm{T}}, \quad \operatorname{rank}\left(\mathbf{N}_2 \mathbf{S}_2\right) = \operatorname{rank}\left(\begin{bmatrix} 1 & -6 \\ -5 & -4 \end{bmatrix}^{\mathrm{T}} \right) = 2. \tag{4.45b}$$

The experimental extents $\tilde{x}_{r,1}$ and $\tilde{x}_{r,2}$ are computed from Eq. (4.38) as:

$$\tilde{x}_{r,1} = V \tilde{y}_1 - \mathbf{s}_1^{\mathrm{T}} \left(\mathbf{W}_{in} \mathbf{x}_{in} + \mathbf{n}_0 \right), \tag{4.46a}$$

$$\tilde{x}_{r,2} = -5/34 \left(V \tilde{y}_2 - \mathbf{s}_2^{\mathrm{T}} \left(\mathbf{W}_{in} \mathbf{x}_{in} + \mathbf{n}_0 \right) \right) - 1/34 \left(V \tilde{y}_3 - \mathbf{s}_3^{\mathrm{T}} \left(\mathbf{W}_{in} \mathbf{x}_{in} + \mathbf{n}_0 \right) \right), \tag{4.46b}$$

which results from

$$\mathscr{T}_{r,1} = \left(\mathbf{N}_1\mathbf{S}_1\mathbf{S}_1^{\mathrm{T}}\mathbf{N}_1^{\mathrm{T}}\right)^{-1}\mathbf{N}_1\mathbf{S}_1 = 1, \qquad \mathbf{e}_1^{\mathrm{T}} = 1, \tag{4.47a}$$

$$\mathscr{T}_{r,2} = \left(\mathbf{N}_2\mathbf{S}_2\mathbf{S}_2^{\mathrm{T}}\mathbf{N}_2^{\mathrm{T}}\right)^{-1}\mathbf{N}_2\mathbf{S}_2 = \begin{bmatrix} \frac{2}{17} & -\frac{3}{17} \\ -\frac{5}{34} & -\frac{1}{34} \end{bmatrix}, \quad \mathbf{e}_2^{\mathrm{T}} = \begin{bmatrix} 0 & 1 \end{bmatrix}. \tag{4.47b}$$

Since the measurements $\tilde{y}_w$ are uncorrelated for all $w = 1,\ldots,W$, the condition in Eq. (4.34) is satisfied, and the extents $\tilde{x}_{r,1}$ and $\tilde{x}_{r,2}$ are uncorrelated.

4.3.2 Toward unbiased rate estimates

As mentioned before, the use of biased rate estimates in the incremental approach may lead to bias in the parameter estimates. Hence, the goal of this section is to compute rate estimates from measurements in a way that removes this bias as much as possible, ideally resulting in unbiased rate estimates.

4.3.2.1 Iterative bias reduction

To be more precise, this section describes a way of iteratively generating a lesser and lesser biased estimate $\hat{r}$ of the rate r from the noisy measurement $\tilde{z}$ of the true variable z. The measurement $\tilde{z}$ corresponds to a unique realization of the random variable Z that follows a normal distribution with known variance σ^2 and mean z (assuming that $\tilde{z}$ is corrupted by additive zero-mean Gaussian noise). Hence, the estimator $\hat{r}(Z)$ should satisfy the condition

$$\mathrm{E}\left[\hat{r}(Z)|Z \sim \mathscr{N}(z,\sigma^2)\right] \approx r(z). \tag{4.48}$$

The bias associated with the estimator $\hat{r}(Z)$, which depends on z, is denoted as $\mathrm{B}_{\hat{r}}(z)$:

$$\mathrm{B}_{\hat{r}}(z) = \mathrm{E}\left[\hat{r}(Z)|Z \sim \mathscr{N}(z,\sigma^2)\right] - r(z). \tag{4.49}$$

Since the bias is typically nonzero, we want to reduce it as much as possible. However, since the bias is a function of the unknown true value z, it may not be possible to remove it exactly. Yet, it is possible to approximate this unknown bias by using the fictitious random variable $\tilde{Z}$, whose mean is the measurement $\tilde{z}$. The interesting feature of the estimator $\hat{r}(\tilde{Z})$ is that its bias,

$$\mathrm{B}_{\hat{r}}(\tilde{z}) = \mathrm{E}\left[\hat{r}(\tilde{Z})|\tilde{Z} \sim \mathscr{N}(\tilde{z},\sigma^2)\right] - r(\tilde{z}), \tag{4.50}$$

is known. By using this expression to approximate the true bias, it is possible to iteratively refine the estimator $\hat{r}(Z)$ by constructing estimators of increasing order.

Let $\hat{r}^n(Z)$ denote the n^{th}-order estimator of $r(z)$. Given $\tilde{z}$, the corresponding estimate of

$r(z)$ is

$$\hat{r}^n(\tilde{z}) = \sum_{j=1}^{n} (-1)^{j+1} \binom{n}{j} \mathscr{E}_j(\tilde{z}), \tag{4.51}$$

with the function $\mathscr{E}_j(x)$ defined recursively as

$$\mathscr{E}_1(x) = r(x), \tag{4.52a}$$
$$\mathscr{E}_j(x) = \mathrm{E}\left[\mathscr{E}_{j-1}(X) | X \sim \mathcal{N}(x, \sigma^2)\right], \qquad j = 2, 3, \ldots. \tag{4.52b}$$

In particular, the first-order and second-order estimates are given by

$$\hat{r}^1(\tilde{z}) = r(\tilde{z}), \tag{4.53a}$$
$$\hat{r}^2(\tilde{z}) = 2r(\tilde{z}) - \mathrm{E}\left[r(\tilde{Z}) | \tilde{Z} \sim \mathcal{N}(\tilde{z}, \sigma^2)\right]. \tag{4.53b}$$

The idea behind the construction of the estimator $\hat{r}^n(Z)$ is that, for each estimate $\hat{r}^n(\tilde{z})$, one uses $\mathrm{B}_{\hat{r}^n}(\tilde{z})$ to approximate $\mathrm{B}_{\hat{r}^n}(z)$ and reduce the bias as follows:

$$\hat{r}^{n+1}(\tilde{z}) = \hat{r}^n(\tilde{z}) - \mathrm{B}_{\hat{r}^n}(\tilde{z}). \tag{4.54}$$

Appendix C.2 shows that this idea results in the estimator presented in Eq. (4.51).

Since this estimator is based on approximating the true bias $\mathrm{B}_{\hat{r}^n}(z)$ by $\mathrm{B}_{\hat{r}^n}(\tilde{z})$, the question remains whether increasing the order of the estimator reduces the true bias. It turns out that there is no general answer to this question, as it actually depends on the rate r. However, if the functional expression of the rate r is known, one can compute $\mathrm{B}_{\hat{r}^n}(z)$ for all the relevant values of z via simulation and check how much of the bias is reduced when the order increases, as illustrated by the example at the end of this subsection. At this point, it is useful to keep in mind that, in the context of the incremental approach, r is a *rate candidate* with known functional expression and need not be the (unknown) true reaction rate. This means that all the assumptions required for the procedure in this section hold.

Another question regards the computation of the function $\mathscr{E}_j(x)$. For this, let F_{x,σ^2} denote the cumulative distribution function of the random variable $X \sim \mathcal{N}(x, \sigma^2)$ and let F^{-1}_{x,σ^2} denote the corresponding inverse distribution function. Upon discretization of the distribution of X by determining D percentiles X_i such that

$$F_{x,\sigma^2}(X_i) = \mathrm{P}\left[X \leq X_i | X \sim \mathcal{N}(x, \sigma^2)\right] = \frac{i - 1/2}{D}, \qquad i = 1, \ldots, D, \tag{4.55}$$

$\mathscr{E}_j(x)$ can be approximated by

$$\mathscr{E}_1(x) = r(x), \tag{4.56a}$$

$$\mathscr{E}_j(x) \simeq \frac{\sum_{i=1}^{D} \mathscr{E}_{j-1}(X_i)}{D} = \frac{\sum_{i=1}^{D} \mathscr{E}_{j-1}\left(F^{-1}_{x,\sigma^2}\left(\frac{i-1/2}{D}\right)\right)}{D}, \qquad j = 2,3,\ldots. \tag{4.56b}$$

Note that, due to the recursive definition of $\mathscr{E}_j(x)$, its computation requires the computation of r at D^{j-1} different points.

Remark 4.7. The delta method is typically used to compute the moments of a function of a random variable (for example the first moment that corresponds to the expected value) [106]. Appendix C.3 shows that the delta method is a particular case of the method presented here. To be more precise, the estimator $\hat{r}^{\delta}(Z)$ that results from the delta method corresponds to $\hat{r}^2(Z)$.

4.3.2.2 Example

The effect of the proposed iterative method for bias reduction is illustrated next. Let us consider the rate $r(z) = \frac{z}{1+z}$ and assume that, in various experiments, the variable z takes the values 0.1, 0.2, ..., 0.9, 1, 1.2, ..., 2.8, 3, 3.4, ..., 5. For each value of z, the random variable Z follows a normal distribution with mean z and variance $\sigma^2 = 0.01$. Since the distribution $Z \sim \mathcal{N}(z, \sigma^2)$ is completely known at simulation time, one can compute the values of $\mathrm{E}\left[\hat{r}^1(Z)\right]$, $\mathrm{E}\left[\hat{r}^2(Z)\right]$, $\mathrm{E}\left[\hat{r}^3(Z)\right]$ and $\mathrm{E}\left[\hat{r}^{\delta}(Z)\right]$ and compare these values to $r(z)$, for each value of z. The bias of each estimator is given by Eq. (4.49). Since $\hat{r}^1(Z)$ is expected to be the estimator with the largest bias, one can compute the ratio between the bias of each subsequent estimator and $\hat{r}^1(Z)$, which has to be less than 1 to ensure bias reduction.

The result of this procedure is shown in Figure 4.1. The most important observation is the fact that the estimators $\hat{r}^2(Z)$, $\hat{r}^3(Z)$ and $\hat{r}^{\delta}(Z)$ provide a bias reduction of 1.5 to 3 orders of magnitude compared to $\hat{r}^1(Z)$, and this for all values of z. Furthermore, it is possible to verify that all the estimators have a similar standard deviation (results not shown). Note that, due to the discretization of the distribution that is required to compute the expected values, $\mathrm{E}\left[\hat{r}^{\delta}(Z)\right]$ and $\mathrm{E}\left[\hat{r}^2(Z)\right]$ seem to be slightly different, but this difference reduces with a finer discretization. It is also possible to observe that $\hat{r}^3(Z)$ is the estimator that leads to the smallest bias.

4.3.3 Maximum-likelihood parameter estimation

As shown in Appendix C.4, if one can write $r_\ell\left(\mathbf{z}(t), \boldsymbol{\theta}\right)$ and its estimate $\hat{r}_\ell\left(\tilde{\mathbf{z}}(t), \boldsymbol{\theta}\right)$ computed according to Section 4.3.2 as weighted sums of products of functions of only one

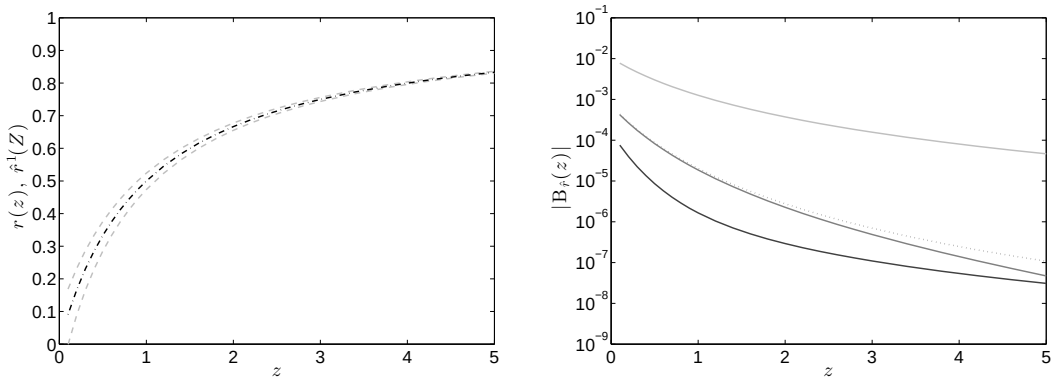

Figure 4.1 – Performance of various rate estimators $\hat{r}^n(Z)$ for $z \in [0.1, \cdots, 5]$. Left: Expected value of the estimator $\hat{r}^1(Z) \pm$ one standard deviation (represented by the dashed lines in light gray) compared to $r(z)$ (dashed-dotted line in black). Right: bias of $\hat{r}^1(Z)$ (in light gray), $\hat{r}^2(Z)$ (in gray), $\hat{r}^3(Z)$ (in dark gray) and $\hat{r}^\delta(Z)$ (dotted line in gray), using a logarithmic scale.

state, that is,

$$r_\ell\big(\mathbf{z}(t), \boldsymbol{\theta}\big) = \sum_{j=1}^{J} w_{\ell,j} \prod_{s=1}^{S+1} r_{\ell,j,s}(z_s(t), \boldsymbol{\theta}), \qquad \forall \ell = 0, \ldots, L, \tag{4.57a}$$

$$\hat{r}_\ell\big(\tilde{\mathbf{z}}(t), \boldsymbol{\theta}\big) = \sum_{j=1}^{J} w_{\ell,j} \prod_{s=1}^{S+1} \hat{r}_{\ell,j,s}\big(\tilde{z}_s(t), \boldsymbol{\theta}\big), \qquad \forall \ell = 0, \ldots, L, \tag{4.57b}$$

and all the measurements $\tilde{\mathbf{z}}(t)$ needed to compute $\hat{r}_\ell\big(\tilde{\mathbf{z}}(t), \boldsymbol{\theta}\big)$ are uncorrelated and corrupted by zero-mean noise, then $\hat{r}_\ell\big(\tilde{\mathbf{z}}(t), \boldsymbol{\theta}\big)$ is an unbiased estimate of $r_\ell\big(\mathbf{z}(t), \boldsymbol{\theta}\big)$, and

$$\lim_{h \to 0} \hat{d}_\ell(t, \boldsymbol{\theta}) = d_\ell(t, \boldsymbol{\theta}), \qquad \forall \ell = 0, \ldots, L. \tag{4.58}$$

From Eqs. (4.11), (4.17), (4.38) and (4.58), one can write:

$$\begin{aligned}
&\lim_{h \to 0} J(\boldsymbol{\alpha}, \boldsymbol{\theta}) \\
&= \sum_{m=1}^{H} \left(d_0(t_m, \boldsymbol{\theta}) + \sum_{\ell=1}^{L} \alpha_\ell d_\ell(t_m, \boldsymbol{\theta}) - \frac{\tilde{x}_{r,i}(t_m)}{V(t_m)} \right)^2 \\
&= \sum_{m=1}^{H} \left(\frac{x_r(t_m, \boldsymbol{\alpha}, \boldsymbol{\theta})}{V(t_m)} - \mathbf{t}_{r,i}^{*\mathrm{T}} \left(\tilde{\mathbf{y}}_i(t_m) - \mathbf{S}_i^{\mathrm{T}} \left(\mathbf{W}_{in} \frac{\mathbf{x}_{in}(t_m)}{V(t_m)} + \mathbf{n}_0 \frac{x_{ic}(t_m)}{V(t_m)} \right) \right) \right)^2,
\end{aligned} \tag{4.59}$$

which implies that, if (i) $\tilde{\mathbf{y}}_i(t)$ follows a multivariate normal distribution, (ii) $\mathbf{t}_{r,i}^{*\mathrm{T}}$ is obtained as shown in Section 4.3.1 such that the experimental extent $\tilde{x}_{r,i}(t)$ is uncorrelated with the other experimental extents, and (iii) r is the i^{th} reaction rate, then the minimization of

$J(\boldsymbol{\alpha}, \boldsymbol{\theta})$ corresponds to the maximum-likelihood estimation of the parameters $\boldsymbol{\alpha}$ and $\boldsymbol{\theta}$ when $h \to 0$. Note that this result is possible if and only if unbiased rate estimates are available.

Remark 4.8. Appendix C.5 shows that, when r is the i^{th} reaction rate and the sampling period h tends to zero (that is, when the number of samples tends to infinity), the global minimum of $J(\boldsymbol{\alpha}, \boldsymbol{\theta})$ is reached for the true parameter values, thus convergence to the global minimum of $J(\boldsymbol{\alpha}, \boldsymbol{\theta})$ is required to compute these true values. In practice, the sampling period is not zero, but if it is small enough, then $\text{PE}_\ell(t, \boldsymbol{\theta}) \approx 0$ and $\text{IE}_\ell(t, \boldsymbol{\theta}) \approx 0$, which implies that $\hat{d}_\ell(t, \boldsymbol{\theta}) \approx d_\ell(t, \boldsymbol{\theta})$, for all $\ell = 0, \ldots, L$. In that case, nearly all the error in $J(\boldsymbol{\alpha}, \boldsymbol{\theta})$ in Eq. (4.59) stems from measurement noise in $\tilde{\mathbf{y}}_i(t)$, which implies that the difference between the maximum-likelihood parameter estimates and the parameter values that correspond to the global minimum of $J(\boldsymbol{\alpha}, \boldsymbol{\theta})$ is negligible. However, Problem (4.22) may have several local minima. Since this optimization problem is unconstrained, the existence of more than one local minimum is a sufficient condition for having the gradients in Eq. (4.23) equal to zero in more than one point. This means that a gradient-based optimization algorithm can only guarantee convergence to global optimality if there is a single local minimum. In addition, with the approach shown above, the functions $\hat{d}_0(t, \boldsymbol{\theta}), \ldots, \hat{d}_L(t, \boldsymbol{\theta})$ need to be computed at each iteration since $\boldsymbol{\theta}$ varies. Section 4.4 will present a convex version of the extent-based incremental approach that overcomes these problems.

4.3.4 Example

This example illustrates the fact that unbiased rate estimates are necessary for reducing bias in parameter estimation.

Consider a batch reactor of constant volume V, where a species with concentration c is consumed according to a second-order kinetic law. This system is described by the dynamical equation

$$\dot{c}(t) = -kc(t)^2, \qquad c(0) = \frac{n_0}{V} = 5 \text{ kmol m}^{-3}, \tag{4.60}$$

with $k = 0.25$ m^3 kmol^{-1} h^{-1}. The extent of reaction can be written as

$$\dot{x}_r(t) = V\, r\big(c(t), k\big) = V\, kc(t)^2, \tag{4.61}$$

which gives:

$$x_r(t) = V \int_0^t kc(\tau)^2 \mathrm{d}\tau. \tag{4.62}$$

Let us assume that the reaction is conducted for 10 h, which results in the concentration profile $c(t)$ shown in Figure 4.2. Measurements $\tilde{c}$ of the true concentrations are available, and they are corrupted by zero-mean Gaussian noise with standard deviation equal to 0.1 kmol m^{-3}. The goal of this identification problem is to estimate k from measurements.

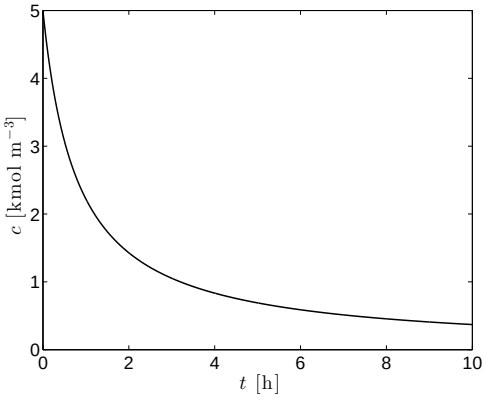

Figure 4.2 – True concentration profile $c(t)$ of a species that varies according to Eq. (4.60).

Three sets of simulated measurements, each with 100 realizations of measurement noise, are available for three different sampling periods h: the first for $h = 12$ s, which is equivalent to a total of $\frac{10\times3600}{12} = 3000$ samples for each realization; the second for $h = 3$ s (12000 samples); the third for $h = 1$ s (36000 samples).

An estimate $\hat{k}$ is obtained for each realization, by using $\hat{r}^1(\tilde{z})$ for rate estimation and applying the incremental model identification method. For each different sampling period, the corresponding 100 estimates $\hat{k}$ are plotted in a histogram. The left-hand side of Figure 4.3 shows the histograms for $h = 12$ s, $h = 3$ s, and $h = 1$ s. One can see that the value of $\hat{k}$ exceeds the true value of $k = 0.25$ m^3 kmol^{-1} h^{-1} in 14 realizations for $h = 12$ s, in 1 realization for $h = 3$ s, and in 0 realizations for $h = 1$ s.

The use of the rate estimate $\hat{r}^1(\tilde{z})$ for kinetic model identification leads to the biased estimate $\hat{k}$, and this for any sampling period. Furthermore, a smaller sampling period does not affect the bias but reduces the standard deviation, with the estimate becoming more precisely centered around its biased mean.

These observations motivate the use of another rate estimator to reduce the bias in rate estimation and thus also in parameter estimation. In particular, it is possible to assess the effect of using $\hat{r}^2(\tilde{z})$ instead of $\hat{r}^1(\tilde{z})$ for the same sets of simulated measurements. The estimates $\hat{k}$ are obtained again for each realization, now by using $\hat{r}^2(\tilde{z})$ for rate estimation and applying the incremental model identification method. For each sampling period, the corresponding 100 estimates $\hat{k}$ are plotted in a histogram. The right-hand side of Figure 4.3 shows the histograms for $h = 12$ s, $h = 3$ s, and $h = 1$ s. In addition, Table 4.1 compares the values of the sample mean, the sample standard deviation and the sample bias of $\hat{k}$ that are obtained by using the two rate estimators for $h = 12$ s, $h = 3$ s, and $h = 1$ s.

These results show that the use of the rate estimator $\hat{r}^2(\tilde{z})$ for kinetic model identification leads to a significant bias reduction, for any sampling period. Furthermore, a smaller sampling period still reduces the standard deviation of $\hat{k}$. With an estimator more precisely

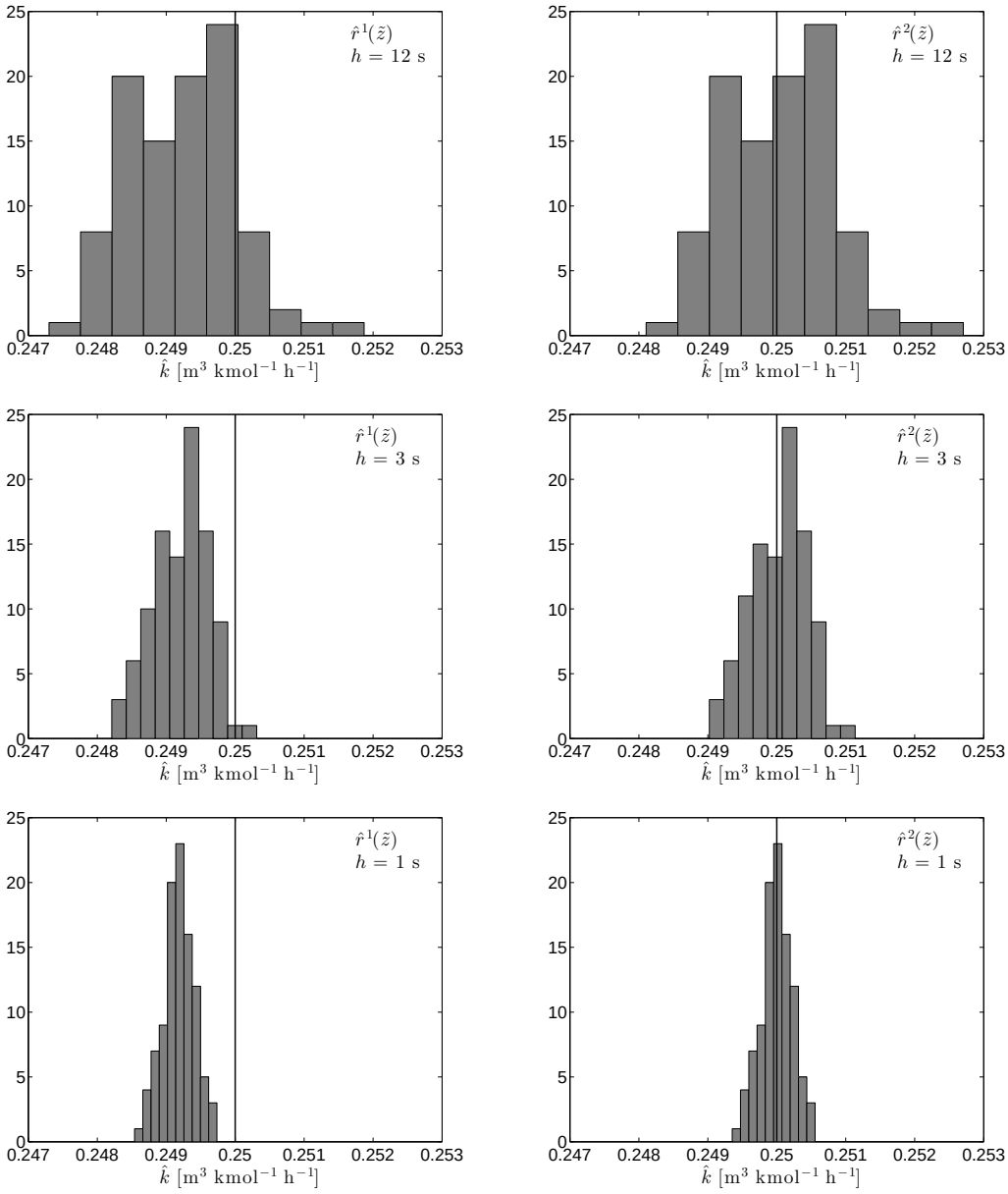

Figure 4.3 – Histogram of the estimate $\hat{k}$ for 100 realizations of measurement noise with sampling periods of 12 s (top), 3 s (middle) and 1 s (bottom), using $\hat{r}^1(\tilde{z})$ (at left) and $\hat{r}^2(\tilde{z})$ (at right) for rate estimation.

Table 4.1 – Estimation of k. Sample mean (s.m.), sample standard deviation (s.s.d.) and sample bias of $\hat{k}$ (that is, the difference between the sample mean and the true value), in $\mathrm{m}^3\ \mathrm{kmol}^{-1}\ \mathrm{h}^{-1}$, for 100 realizations of measurement noise with sampling periods of 12 s, 3 s, and 1 s, using $\hat{r}^1(\tilde{z})$ and $\hat{r}^2(\tilde{z})$ for rate estimation.

h [s]	Using $\hat{r}^1(\tilde{z})$		Using $\hat{r}^2(\tilde{z})$	
	S.m.±s.s.d. of $\hat{k}$	S.m. of $\hat{k}-k$	S.m.±s.s.d. of $\hat{k}$	S.m. of $\hat{k}-k$
12	0.24924 ± 0.00079	-7.591×10^{-4}	0.25006 ± 0.00079	0.587×10^{-4}
3	0.24920 ± 0.00041	-7.957×10^{-4}	0.25002 ± 0.00041	0.217×10^{-4}
1	0.24918 ± 0.00023	-8.196×10^{-4}	0.25000 ± 0.00023	-0.024×10^{-4}

centered around a mean that is very close to the true value, the estimate $\hat{k}$ appears to be consistent. Note that this example has clearly illustrated that the use of biased rate estimators in incremental model identification can lead to biased parameter estimation.

4.4 Globally Optimal Estimation via the Extent-based Incremental Approach

This section presents a method that solves to global optimality the identification problem resulting from the extent-based incremental approach.

4.4.1 Taylor series expansion of the rate law

Let us consider the rate law given in Section 4.2.2. The rate r can be written as a multivariate Taylor series if $r_0, \ldots, r_L$ are infinitely differentiable functions and there exists a vector $\bar{\boldsymbol{\theta}}$ and a set $\mathscr{P}$ such that the Taylor series converges $\forall \Delta\boldsymbol{\theta} \in \mathscr{P}$, that is,

$$\lim_{n\to\infty} \sum_{\mathbf{k}\in\mathscr{K}_n} \frac{1}{\mathbf{k}!} \frac{\partial^{\mathbf{k}} r}{\partial \boldsymbol{\theta}^{\mathbf{k}}}\big(\mathbf{z}(t), \boldsymbol{\alpha}, \bar{\boldsymbol{\theta}}\big) \Delta\boldsymbol{\theta}^{\mathbf{k}} \neq \infty, \quad \forall \Delta\boldsymbol{\theta} \in \mathscr{P}, \tag{4.63}$$

where $\Delta\boldsymbol{\theta} := \boldsymbol{\theta} - \bar{\boldsymbol{\theta}}$ is the deviation of $\boldsymbol{\theta}$ around $\bar{\boldsymbol{\theta}}$, $\mathbf{k} := (k_1, \ldots, k_N)$ is the vector of monomial powers, the set $\mathscr{K}_n := \big\{(k_1, \ldots, k_N) \in \mathbb{N}_0^N : 0 \leq k_1 + \ldots + k_N \leq n\big\}$ in the case of a polynomial of degree n, $\mathbf{k}! := k_1! \ldots k_N!$, $\Delta\boldsymbol{\theta}^{\mathbf{k}} := \big(\theta_1 - \bar{\theta}_1\big)^{k_1} \ldots \big(\theta_N - \bar{\theta}_N\big)^{k_N}$, and $\frac{\partial^{\mathbf{k}}}{\partial \boldsymbol{\theta}^{\mathbf{k}}} := \frac{\partial^{k_1+\ldots+k_N}}{\partial \theta_1^{k_1} \ldots \partial \theta_N^{k_N}}$.

The reaction rate r can be represented as a Taylor series with respect to the parameters $\boldsymbol{\theta}$:

$$r\big(\mathbf{z}(t), \boldsymbol{\alpha}, \boldsymbol{\theta}\big) = \lim_{n\to\infty} \sum_{\mathbf{k}\in\mathscr{K}_n} \frac{1}{\mathbf{k}!} \left(\frac{\partial^{\mathbf{k}} r_0}{\partial \boldsymbol{\theta}^{\mathbf{k}}}\big(\mathbf{z}(t), \bar{\boldsymbol{\theta}}\big) + \sum_{\ell=1}^{L} \alpha_\ell \frac{\partial^{\mathbf{k}} r_\ell}{\partial \boldsymbol{\theta}^{\mathbf{k}}}\big(\mathbf{z}(t), \bar{\boldsymbol{\theta}}\big) \right) \Delta\boldsymbol{\theta}^{\mathbf{k}}, \quad \forall \Delta\boldsymbol{\theta} \in \mathscr{P}. \tag{4.64}$$

Note that $\bar{\boldsymbol{\theta}}$ is not an initial guess for $\boldsymbol{\theta}$, but it should be chosen such that the Taylor series converges for all the possible optimal values of $\boldsymbol{\theta}$. This convergence can be easily verified from the knowledge of the functional expression of r. This is illustrated in the following example.

Example – Michaelis-Menten kinetics

Consider a Michaelis-Menten rate law for an isothermal reaction:

$$r\big(z(t),\alpha,\theta\big)=\alpha r_1\big(z(t),\theta\big)=\alpha\frac{z(t)}{\theta+z(t)}, \tag{4.65}$$

where $z(t)$ represents the concentration of substrate, $\alpha=V_{max}$ and $\theta=K_m$, with V_{max} the maximal rate and K_m the Michaelis constant.

This rate expression yields

$$\tfrac{\partial^k r}{\partial\theta^k}\big(z(t),\alpha,\theta\big)=\alpha\frac{z(t)(-1)^k\,k!}{(\theta+z(t))^{k+1}} \tag{4.66}$$

and

$$\tfrac{1}{k!}\tfrac{\partial^k r}{\partial\theta^k}\big(z(t),\alpha,\bar{\theta}\big)\Delta\theta^k=\alpha\frac{z(t)(-1)^k\,k!}{\big(\bar{\theta}+z(t)\big)^{k+1}k!}\Delta\theta^k=\alpha\frac{z(t)}{\bar{\theta}+z(t)}\left(-\frac{\Delta\theta}{\bar{\theta}+z(t)}\right)^k. \tag{4.67}$$

Since it is known that $z(t)\geq 0$, the approach above is applicable if a constant $\bar{\theta}>0$ can be chosen such that $\Delta\theta\in\mathscr{P}=\left]-\bar{\theta},\bar{\theta}\right[$, because $\left|-\frac{\Delta\theta}{\bar{\theta}+z(t)}\right|<1$ in that case. This implies that, for all $\Delta\theta\in\mathscr{P}=\left]-\bar{\theta},\bar{\theta}\right[$, the Taylor series converges since

$$\lim_{n\to\infty}\sum_{k=0}^{n}\tfrac{1}{k!}\tfrac{\partial^k r}{\partial\theta^k}\big(z(t),\alpha,\bar{\theta}\big)\Delta\theta^k=\alpha\frac{z(t)}{\bar{\theta}+z(t)}\lim_{n\to\infty}\left(\sum_{k=0}^{n}\left(-\frac{\Delta\theta}{\bar{\theta}+z(t)}\right)^k\right)\neq\infty. \tag{4.68}$$

4.4.2 Approximate identification problem

From Eqs. (4.11) and (4.64), the vessel extent of reaction is

$$x_r(t,\boldsymbol{\alpha},\boldsymbol{\theta})=\lim_{n\to\infty}\sum_{\mathbf{k}\in\mathscr{K}_n}V(t)\,d_{0,\mathbf{k}}(t)\Delta\boldsymbol{\theta}^{\mathbf{k}}+\sum_{\ell=1}^{L}\alpha_\ell\sum_{\mathbf{k}\in\mathscr{K}_n}V(t)\,d_{\ell,\mathbf{k}}(t)\Delta\boldsymbol{\theta}^{\mathbf{k}},\quad\forall\Delta\boldsymbol{\theta}\in\mathscr{P}, \tag{4.69}$$

where

$$d_{\ell,\mathbf{k}}(t):=\int_0^t\tfrac{1}{\mathbf{k}!}\tfrac{\partial^{\mathbf{k}}r_\ell}{\partial\boldsymbol{\theta}^{\mathbf{k}}}\big(\mathbf{z}(\tau),\bar{\boldsymbol{\theta}}\big)\tfrac{x_{ic}(t)/V(t)}{x_{ic}(\tau)/V(\tau)}\mathrm{d}\tau,\qquad\forall\ell=0,\ldots,L,\qquad\forall\mathbf{k}\in\mathscr{K}_n. \tag{4.70}$$

In practice, upon numerical integration and replacing $\frac{\partial^{\mathbf{k}} r_\ell}{\partial \boldsymbol{\theta}^{\mathbf{k}}}\big(\mathbf{z}(t_m), \bar{\boldsymbol{\theta}}\big)$ by its estimate $\hat{r}_{\ell,\mathbf{k}}\big(\tilde{\mathbf{z}}(t_m)\big)$, $d_{\ell,\mathbf{k}}(t)$ is approximated by

$$\hat{d}_{\ell,\mathbf{k}}(t) := \sum_{m=0}^{\frac{t}{h}} h\gamma_m \tfrac{1}{\mathbf{k}!}\, \hat{r}_{\ell,\mathbf{k}}\big(\tilde{\mathbf{z}}(t_m)\big) \tfrac{x_{ic}(t)/V(t)}{x_{ic}(t_m)/V(t_m)}, \qquad \forall \ell = 0,\dots,L, \qquad \forall \mathbf{k} \in \mathscr{K}_n. \quad (4.71)$$

It follows from the definitions of the propagation and integration errors in Remark 4.1 (which would be analogous in this case) that:

$$\hat{d}_{\ell,\mathbf{k}}(t) - d_{\ell,\mathbf{k}}(t) = \mathrm{PE}_{\ell,\mathbf{k}}(t) + \mathrm{IE}_{\ell,\mathbf{k}}(t), \qquad \forall \ell = 0,\dots,L, \qquad \forall \mathbf{k} \in \mathscr{K}_n. \quad (4.72)$$

If r is a rate candidate for the i^{th} reaction, this leads to the identification problem

$$\min_{\boldsymbol{\alpha},\Delta\boldsymbol{\theta}} J_c(\boldsymbol{\alpha},\Delta\boldsymbol{\theta}) = \sum_{m=1}^{H} \left(\frac{\hat{x}_r(t_m,\boldsymbol{\alpha},\Delta\boldsymbol{\theta}) - \tilde{x}_{r,i}(t_m)}{V(t_m)} \right)^2, \quad (4.73)$$

with $\hat{x}_r(t_m,\boldsymbol{\alpha},\Delta\boldsymbol{\theta}) := \sum_{\mathbf{k}\in\mathscr{K}_n} V(t_m)\,\hat{d}_{0,\mathbf{k}}(t_m)\Delta\boldsymbol{\theta}^{\mathbf{k}} + \sum_{\ell=1}^{L} \alpha_\ell \sum_{\mathbf{k}\in\mathscr{K}_n} V(t_m)\,\hat{d}_{\ell,\mathbf{k}}(t_m)\Delta\boldsymbol{\theta}^{\mathbf{k}}$ for finite n.

4.4.3 Reformulation as a polynomial optimization problem

The cost function in Eq. (4.73) is quadratic in $\boldsymbol{\alpha}$, that is,

$$J_c(\boldsymbol{\alpha},\Delta\boldsymbol{\theta}) = c_c(\Delta\boldsymbol{\theta}) + 2\boldsymbol{\alpha}^{\mathrm{T}}\mathbf{g}_c(\Delta\boldsymbol{\theta}) + \boldsymbol{\alpha}^{\mathrm{T}}\mathbf{H}_c(\Delta\boldsymbol{\theta})\boldsymbol{\alpha}, \quad (4.74)$$

where the elements of $c_c(\Delta\boldsymbol{\theta})$, $\mathbf{g}_c(\Delta\boldsymbol{\theta})$ and $\mathbf{H}_c(\Delta\boldsymbol{\theta})$ are polynomials of degree $2n$ in $\Delta\boldsymbol{\theta}$ with coefficients computed analytically from $\hat{d}_{0,\mathbf{k}}(t_m)$, …, $\hat{d}_{L,\mathbf{k}}(t_m)$ and $\frac{\tilde{x}_{r,i}(t_m)}{V(t_m)}$, as follows:

$$c_c(\Delta\boldsymbol{\theta}) = \sum_{m=1}^{H} \left(\sum_{\mathbf{k}\in\mathscr{K}_n} \hat{d}_{0,\mathbf{k}}(t_m)\Delta\boldsymbol{\theta}^{\mathbf{k}} - \frac{\tilde{x}_{r,i}(t_m)}{V(t_m)} \right)^2, \quad (4.75a)$$

$$\mathbf{g}_c(\Delta\boldsymbol{\theta}) = \sum_{m=1}^{H} \left(\sum_{\mathbf{k}\in\mathscr{K}_n} \hat{\mathbf{d}}_{\mathbf{k}}(t_m)\Delta\boldsymbol{\theta}^{\mathbf{k}} \right) \left(\sum_{\mathbf{k}\in\mathscr{K}_n} \hat{d}_{0,\mathbf{k}}(t_m)\Delta\boldsymbol{\theta}^{\mathbf{k}} - \frac{\tilde{x}_{r,i}(t_m)}{V(t_m)} \right), \quad (4.75b)$$

$$\mathbf{H}_c(\Delta\boldsymbol{\theta}) = \sum_{m=1}^{H} \left(\sum_{\mathbf{k}\in\mathscr{K}_n} \hat{\mathbf{d}}_{\mathbf{k}}(t_m)\Delta\boldsymbol{\theta}^{\mathbf{k}} \right) \left(\sum_{\mathbf{k}\in\mathscr{K}_n} \hat{\mathbf{d}}_{\mathbf{k}}(t_m)\Delta\boldsymbol{\theta}^{\mathbf{k}} \right)^{\mathrm{T}}, \quad (4.75c)$$

where $\hat{\mathbf{d}}_{\mathbf{k}}(t_m) := \begin{bmatrix} \hat{d}_{1,\mathbf{k}}(t_m) & \cdots & \hat{d}_{L,\mathbf{k}}(t_m) \end{bmatrix}^{\mathrm{T}}$. Note that $\mathbf{H}_c(\Delta\boldsymbol{\theta})$ is invertible since $\mathbf{H}_c(\Delta\boldsymbol{\theta}) \succ \mathbf{0}_{L\times L}$.

The optimal parameters $\boldsymbol{\alpha}$ can be computed for each $\Delta\boldsymbol{\theta}$ as

$$\hat{\boldsymbol{\alpha}}_c(\Delta\boldsymbol{\theta}) = -\mathbf{H}_c(\Delta\boldsymbol{\theta})^{-1}\mathbf{g}_c(\Delta\boldsymbol{\theta}), \tag{4.76}$$

which allows an exact reformulation of the optimization problem described in Eq. (4.73) with only the decision variables $\Delta\boldsymbol{\theta}$:

$$\begin{aligned}\min_{\Delta\boldsymbol{\theta}} \bar{J}_c(\Delta\boldsymbol{\theta}) &= J_c\Big(\hat{\boldsymbol{\alpha}}_c(\Delta\boldsymbol{\theta}), \Delta\boldsymbol{\theta}\Big) = c_c(\Delta\boldsymbol{\theta}) - \mathbf{g}_c(\Delta\boldsymbol{\theta})^{\mathrm{T}}\mathbf{H}_c(\Delta\boldsymbol{\theta})^{-1}\mathbf{g}_c(\Delta\boldsymbol{\theta}) \\ &= \frac{\det\big(\mathbf{M}(\Delta\boldsymbol{\theta})\big)}{\det\big(\mathbf{H}_c(\Delta\boldsymbol{\theta})\big)},\end{aligned} \tag{4.77}$$

with $\mathbf{M}(\Delta\boldsymbol{\theta}) := \begin{bmatrix} c_c(\Delta\boldsymbol{\theta}) & \mathbf{g}_c(\Delta\boldsymbol{\theta})^{\mathrm{T}} \\ \mathbf{g}_c(\Delta\boldsymbol{\theta}) & \mathbf{H}_c(\Delta\boldsymbol{\theta}) \end{bmatrix}$, and where the denominator $P_a(\Delta\boldsymbol{\theta}) := \det\big(\mathbf{H}_c(\Delta\boldsymbol{\theta})\big)$ and the numerator $P_b(\Delta\boldsymbol{\theta}) := \det\big(\mathbf{M}(\Delta\boldsymbol{\theta})\big)$ are polynomials in $\Delta\boldsymbol{\theta}$. The reformulation of $\bar{J}_c(\Delta\boldsymbol{\theta})$ as a rational function is possible since it is the determinant of the Schur complement of $\mathbf{H}_c(\Delta\boldsymbol{\theta})$ in $\mathbf{M}(\Delta\boldsymbol{\theta})$ [80]. One can then write Problem (4.77) as the polynomial optimization problem

$$\max_{\zeta} \quad \zeta \qquad \text{s.t.} \qquad P_b(\Delta\boldsymbol{\theta}) - P_a(\Delta\boldsymbol{\theta})\zeta \geq 0, \ \forall \Delta\boldsymbol{\theta}. \tag{4.78}$$

Remark 4.9. Since the coefficients of $P_a(\Delta\boldsymbol{\theta})$ and $P_b(\Delta\boldsymbol{\theta})$ do not depend on $\Delta\boldsymbol{\theta}$, they do not have to be computed at each iteration. Hence, Problem (4.78) is an algebraic estimation problem. In contrast, other identification methods result in dynamic estimation problems, in the sense that the numerical integration needs to be repeated at each iteration of the optimization algorithm.

4.4.4 Reformulation as a convex optimization problem

Let us denote the coefficients of $P_a(\Delta\boldsymbol{\theta})$ and $P_b(\Delta\boldsymbol{\theta})$ as $a_{\mathbf{k}}$ and $b_{\mathbf{k}}$ such that $P_a(\Delta\boldsymbol{\theta}) = \sum_{\mathbf{k}\in\mathscr{K}_{2d}} a_{\mathbf{k}}\Delta\boldsymbol{\theta}^{\mathbf{k}}$ and $P_b(\Delta\boldsymbol{\theta}) = \sum_{\mathbf{k}\in\mathscr{K}_{2d}} b_{\mathbf{k}}\Delta\boldsymbol{\theta}^{\mathbf{k}}$, with $d \geq n(L+1)$. Appendix C.6 shows that, by using the equivalence of nonnegative polynomials and conical combination of sum-of-squares polynomials on a compact set [102], Problem (4.78) can be written as the convex semidefinite program (SDP) given in Eq. (C.34), with the coefficients $a_{\mathbf{k}}$ and $b_{\mathbf{k}}$, $\forall \mathbf{k} \in \mathscr{K}_{2d}$, being computed only once prior to optimization.

This SDP is constrained by two linear matrix inequalities (LMIs) of sizes $s(N,d)$ and $s(N,d-1)$, where $s(N,d) := \binom{N+d}{d}$. One expects a small problem size since the numbers L and N of model parameters are usually low in the incremental approach. The degree n of the Taylor series should be sufficiently large to allow a good approximation of the rate r, but not too large since, otherwise, the size of the SDP grows too much and the matrices that describe it could become ill-conditioned.

4.4.5 Computing solutions

The SDP (C.34) yields ζ^*, which is equal to the minimum cost $\bar{J}_c(\Delta\boldsymbol{\theta}^*)$, but it does not provide an explicit way of finding the global solution $\Delta\boldsymbol{\theta}^*$ (and thus $\boldsymbol{\alpha}^*$).

For numerical reasons, the solutions to the primal and dual problems should be combined to obtain the best solution $\Delta\boldsymbol{\theta}^*$. Appendix C.7 shows how to compute $\Delta\boldsymbol{\theta}^*$ from these solutions.

Finally, the optimal values $\boldsymbol{\alpha}^* = \hat{\boldsymbol{\alpha}}_c(\Delta\boldsymbol{\theta}^*)$ can be computed according to Eq. (4.76).

4.4.6 Maximum-likelihood parameter estimation

As shown in Appendix C.8, if one can write $\frac{\partial^{\mathbf{k}} r_\ell}{\partial \boldsymbol{\theta}^{\mathbf{k}}}\big(\mathbf{z}(t), \bar{\boldsymbol{\theta}}\big)$ and its estimate $\hat{r}_{\ell,\mathbf{k}}\big(\tilde{\mathbf{z}}(t)\big)$ computed according to Section 4.3.2 as weighted sums of products of functions of only one state, that is,

$$\frac{\partial^{\mathbf{k}} r_\ell}{\partial \boldsymbol{\theta}^{\mathbf{k}}}\big(\mathbf{z}(t), \bar{\boldsymbol{\theta}}\big) = \sum_{j=1}^{J} w_{\ell,\mathbf{k},j} \prod_{s=1}^{S+1} r_{\ell,\mathbf{k},j,s}\big(z_s(t)\big), \qquad \forall \ell = 0,\dots,L, \qquad \forall \mathbf{k} \in \mathscr{K}_n, \tag{4.79a}$$

$$\hat{r}_{\ell,\mathbf{k}}\big(\tilde{\mathbf{z}}(t)\big) = \sum_{j=1}^{J} w_{\ell,\mathbf{k},j} \prod_{s=1}^{S+1} \hat{r}_{\ell,\mathbf{k},j,s}\big(\tilde{z}_s(t)\big), \qquad \forall \ell = 0,\dots,L, \qquad \forall \mathbf{k} \in \mathscr{K}_n, \tag{4.79b}$$

and all the measurements $\tilde{\mathbf{z}}(t)$ needed to compute $\hat{r}_{\ell,\mathbf{k}}\big(\tilde{\mathbf{z}}(t)\big)$ are uncorrelated and corrupted by zero-mean noise, then $\hat{r}_{\ell,\mathbf{k}}\big(\tilde{\mathbf{z}}(t)\big)$ is an unbiased estimate of $\frac{\partial^{\mathbf{k}} r_\ell}{\partial \boldsymbol{\theta}^{\mathbf{k}}}\big(\mathbf{z}(t), \bar{\boldsymbol{\theta}}\big)$, and

$$\lim_{h\to 0} \hat{d}_{\ell,\mathbf{k}}(t) = d_{\ell,\mathbf{k}}(t), \qquad \forall \ell = 0,\dots,L, \qquad \forall \mathbf{k} \in \mathscr{K}_n. \tag{4.80}$$

From Eqs. (4.38), (4.69), (4.73), and (4.80), one can write:

$$\begin{aligned}
&\lim_{n\to\infty} \lim_{h\to 0} J_c(\boldsymbol{\alpha}, \Delta\boldsymbol{\theta}) \\
&= \lim_{n\to\infty} \sum_{m=1}^{H} \left(\sum_{\mathbf{k}\in\mathscr{K}_n} d_{0,\mathbf{k}}(t_m)\Delta\boldsymbol{\theta}^{\mathbf{k}} + \sum_{\ell=1}^{L} \alpha_\ell \sum_{\mathbf{k}\in\mathscr{K}_n} d_{\ell,\mathbf{k}}(t_m)\Delta\boldsymbol{\theta}^{\mathbf{k}} - \frac{\tilde{x}_{r,i}(t_m)}{V(t_m)} \right)^2 \\
&= \sum_{m=1}^{H} \left(\frac{x_r(t_m, \boldsymbol{\alpha}, \boldsymbol{\theta})}{V(t_m)} - \mathbf{t}_{r,i}^{*\mathrm{T}} \left(\tilde{\mathbf{y}}_i(t_m) - \mathbf{S}_i^{\mathrm{T}} \left(\mathbf{W}_{in} \frac{\mathbf{x}_{in}(t_m)}{V(t_m)} + \mathbf{n}_0 \frac{x_{ic}(t_m)}{V(t_m)} \right) \right) \right)^2,
\end{aligned} \tag{4.81}$$

which implies that, if (i) $\tilde{\mathbf{y}}_i(t)$ follows a multivariate normal distribution, (ii) $\mathbf{t}_{r,i}^{*\mathrm{T}}$ is obtained as shown in Section 4.3.1 such that the experimental extent $\tilde{x}_{r,i}(t)$ is uncorrelated with the other experimental extents, (iii) the Taylor series converges for the optimal $\Delta\boldsymbol{\theta}$, and (iv) r is the i^{th} reaction rate, then the minimization of $J_c(\boldsymbol{\alpha}, \Delta\boldsymbol{\theta})$ corresponds to the maximum-likelihood estimation of the parameters $\boldsymbol{\alpha}$ and $\boldsymbol{\theta}$ when $h \to 0$ and n is large enough. Note that this result is possible if and only if unbiased rate estimates are available.

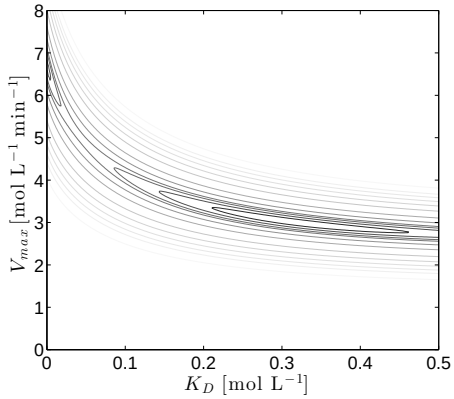

Figure 4.4 – Contour plot of the cost function $J(V_{max}, K_D)$. The contour lines are shown with a decreasing contrast for $J(V_{max}, K_D)$ with increasing values in the set $\{0.03, 0.09, 0.17, 0.25, 0.5, 1, 2, 3, 4, 5, 6, 8, 10\}$.

4.5 Simulated Example

This section illustrates the use of extent-based incremental model identification solved to *global optimality* on a problem that exhibits more than one local minimum. For this, let us consider a batch reactor of constant volume, in which the enzymatic decomposition S $\rightarrow$ 2 I and the product formation I $\rightarrow$ P take place. The objective is to identify the maximal rate V_{max} and the inhibition constant K_D of the enzymatic decomposition. The concentrations of S, I and P are denoted as c_S, c_I and c_P, and $\mathbf{c} = \begin{bmatrix} c_S & c_I & c_P \end{bmatrix}^{\mathrm{T}}$. The stoichiometry is given by $\mathbf{N} = \left[\begin{smallmatrix} -1 & 2 & 0 \\ 0 & -1 & 1 \end{smallmatrix}\right]$. The kinetics of the decomposition reaction expresses the behavior of an enzyme with two binding sites of equal binding affinity, no cooperativity, and previously known substrate inhibition [107]:

$$r(\mathbf{c}, \alpha, \theta) = V_{max} \frac{\frac{c_S}{K_D} + 0.1\frac{c_S^2}{K_D^2}}{1 + 2\frac{c_S}{K_D} + \frac{c_S^2}{K_D^2}}, \tag{4.82}$$

with the parameter $\alpha = V_{max} = 3$ mol L^{-1} min^{-1} appearing linearly and the parameter $\theta = K_D = 0.32$ mol L^{-1} appearing nonlinearly in the rate law, that is, $L = 1$ and $N = 1$. The dynamics of c_S is described by

$$\dot{c}_S = -r(\mathbf{c}, \alpha, \theta), \qquad c_S(0) = c_{S,0} = 2 \text{ mol L}^{-1}. \tag{4.83}$$

An experiment is run for 3 min and noise-free measurements of the concentration c_S are collected every 5 s. If the measurements $\tilde{c}_S$ were corrupted by noise, it would be possible to compute unbiased estimates of $r(\mathbf{c}, \alpha, \theta)$ as shown in Section 4.3.2. In addition, if the measurements $\tilde{c}_P$ were also available, one would be able to compute uncorrelated extents

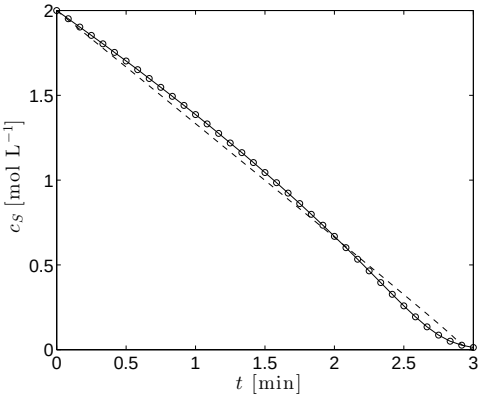

Figure 4.5 – Measured concentrations (circles) and fitted profiles that result from the solution to the identification problem using standard (dashed line) and convex (solid line) optimization algorithms.

$\tilde{x}_{r,1}$ and $\tilde{x}_{r,2}$ according to Section 4.3.1, using

$$\tilde{x}_{r,1} = V\left(c_{S,0} - \tilde{c}_S\right), \tag{4.84a}$$

$$\tilde{x}_{r,2} = V\left(\tilde{c}_P - c_{P,0}\right). \tag{4.84b}$$

The noise-free case is considered here. Even in this case, the contour plot of the identification cost function $J(V_{max}, K_D)$ in Figure 4.4 shows the presence of two local minima. Depending on the initial guess that is used, a standard gradient-based optimization algorithm may not converge to the correct values of the parameters V_{max} and K_D. For example, a standard optimization algorithm with user-supplied gradients and using the initial guess $K_D = 0.04$ mol L^{-1} yields the solution $V^*_{max} = 6.63$ mol L^{-1} min^{-1}, $K^*_D = 0.001$ mol L^{-1}, with $J(V^*_{max}, K^*_D) = 0.0702$. However, the convex optimization algorithm presented in Section 4.4, using $n = 20$ and $\bar{\theta} = 1$ mol L^{-1}, yields the global solution $V^*_{max} = 3$ mol L^{-1} min^{-1}, $K^*_D = 0.32$ mol L^{-1}, with $J(V^*_{max}, K^*_D) = 4.4 \times 10^{-9}$. Figure 4.5 shows that the fitted curves that result from these two solutions are different, and only the convex algorithm predicts a concentration profile that matches the measurements.

In addition, one can simulate the substrate concentration using a different initial condition, that is, $c_{S,0} = 3$ instead of 2 mol L^{-1}. Figure 4.6 shows that the two models are indeed significantly different.

4.6 Conclusion

This chapter has shown that extent-based incremental model identification can be used to converge efficiently to global optimality. Several features of extent-based incremental model identification contribute to this result. Firstly, the cost function that results from this

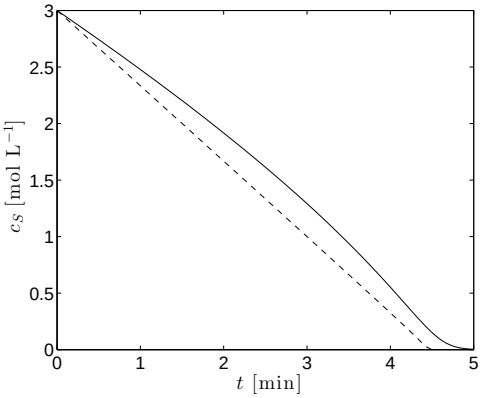

Figure 4.6 – Simulated concentrations with a different initial condition corresponding to the two models that were obtained using standard (dashed line) and convex (solid line) optimization algorithms for model identification.

approach involves only the parameters of a single rate candidate and is a quadratic function of the parameters in which the rate expression is linear. Since these parameters can be determined via matrix inversion, the number of parameters that need to be determined via optimization is much smaller than in identification problems that result from the simultaneous approach. Secondly, this cost function can be approximated via a Taylor series expansion as a rational function of the parameters that appear nonlinearly in the rate expression. This rational function is used in the formulation of the identification problem as a polynomial optimization problem with constant coefficients computed only once prior to optimization. Finally, this polynomial optimization problem can be converted to an SDP, which can be handled by SDP solvers that efficiently attain the global solution upon convergence.

As a consequence, guaranteed convergence to global optimality via the extent-based incremental approach exists for virtually all identification problems in reaction systems, provided that some mild technical conditions are satisfied. For many of these problems, it would be practically infeasible to obtain global optimality via the standard simultaneous approach, due to the large number of model parameters and the many possible combinations of rate candidates. As shown by the simulated example in this chapter, identification problems with more than one local minimum exist, and standard optimization algorithms may converge to a local minimum that is not the global one.

This chapter has also shown that extent-based incremental model identification not only converges to global optimality, but can also be used to provide maximum-likelihood parameter estimates, with quality similar to simultaneous model identification. Maximum-likelihood parameter estimation relies on (i) a method to obtain uncorrelated experimental extents from a set of uncorrelated measurements that depend linearly on these extents, and (ii) a method to obtain unbiased rate estimates computed from measurements corrupted by zero-mean noise. In other words, the experimental extents are computed from

measured concentrations such that they are uncorrelated, whereas the modeled extents correspond to the integral of unbiased rate estimates computed from measured concentrations. Both the computation of uncorrelated experimental extents and the use of unbiased rate estimation contribute decisively to being able to estimate optimal parameters in the maximum-likelihood sense. Future work shall focus on ensuring that uncorrelated experimental extents can be obtained even when the measurements are correlated or depend nonlinearly on the extents.

Another relevant extension of this work is the application of the extent-based incremental approach to reaction systems other than the lumped homogeneous reaction systems considered in this chapter. Since the concept of extents has been developed for other reaction systems, as mentioned in Section 4.2.1, such an extension seems to be relatively straightforward. In general, any reaction system can be described by a model in terms of (ordinary or partial) differential and algebraic equations that express the material and heat balances in the system. These models include reaction rates that can always be written as analytical expressions that relate concentrations and temperature to reaction rates. Hence, the existence of such analytical expressions assumed by the incremental approach does not represent a limitation for the extension of the approach to other systems. The only aspect that might hinder the use of the incremental approach in certain situations is the fact that it requires that the reaction rates be expressed as functions of measured quantities. This is realistic in the case of lumped homogeneous reaction systems but may be difficult in other reaction systems due to experimental constraints. In summary, one can foresee that it will be possible to design an extent-based incremental approach that guarantees globally optimal, maximum-likelihood estimates of kinetic parameters for any reaction system where the reaction rates can be expressed as functions of measured quantities.

5 Estimation of Rate Signals without Kinetic Models

Part of this chapter is adapted from the postprint of the following article [108]:

D. Rodrigues, M. Amrhein, J. Billeter, and D. Bonvin. Fast estimation of plant steady state for imperfectly known dynamic systems, with application to real-time optimization. *Ind. Eng. Chem. Res.*, 57(10):3699–3716, 2018.

Link: http://doi.org/10.1021/acs.iecr.7b04631.

The author of this thesis contributed to that article by developing the main novel ideas, implementing the simulations, and writing a significant part of the text. Hence, the author retains the right to include the article in this thesis since it is not published commercially and the journal is referenced as the original source.

5.1 Introduction

Model identification, controller design, and process optimization are often regarded as closely related tasks since the control laws and the optimal decision policies are typically calculated using the plant model. For example, efficient control of reaction systems typically requires good kinetic models to predict the dynamic effects, namely the reaction rates.

Since the identification of reaction systems can be rather difficult and time consuming, one would ideally like to avoid it as much as possible. Hence, one could try to infer the reaction rates directly from measurements, that is, without the help of a kinetic model, which can be done if the various rates can be decoupled [99]. This decoupling would be an alternative to the use of observers for measurement-based rate estimation without kinetic models [2], the latter being difficult to design due to the coupling between the estimated states and the estimated rates.

The concept of variants and invariants has been proposed to decouple the dynamic effects in reaction systems, thereby facilitating their analysis, control and monitoring [12, 11]. A finer separation of the various dynamic effects in both homogeneous and heterogeneous open reaction systems has been proposed along with a linear transformation of the numbers

of moles and heat to a particular type of variants in chemical reaction systems, the so-called vessel extents [18, 19].

Since the concept of variants allows isolating the different rates in reaction systems, it can also be used to estimate unknown rates without the need for identifying the corresponding (kinetic) models. Subsequently, it is legitimate to ask whether applications of variants to control and optimization can be found.

Regarding the case of reaction systems, this chapter introduces methods that will allow estimating reaction rates from concentration and temperature measurements via the concept of variants, which will be applied in subsequent chapters.

This chapter is structured as follows. The systems considered in this chapter are described in Section 5.2, a numerical differentiation filter that is relevant for the purpose of rate estimation, the Savitzky-Golay filter, is presented in Section 5.3, and the rate estimation method and its properties are shown in Section 5.4, while Section 5.5 concludes this chapter.

5.2 System Description

Let us consider a system with n_u inputs $\mathbf{u}(t)$ and a number of states, from which an n_y-dimensional vector of states $\mathbf{y}(t)$ is available[1]. An additional vector of states that are unavailable may exist, but will not be considered in the following discussion.

Furthermore, in this system, there are n_r rates $\mathbf{r}_u$ whose values are unknown and n_y available rates $\mathbf{s}_a$ whose values are known. These rates may depend on the available states $\mathbf{y}(t)$ and the inputs $\mathbf{u}(t)$, which is represented as $\mathbf{r}_u\big(\mathbf{y}(t),\mathbf{u}(t)\big)$ and $\mathbf{s}_a\big(\mathbf{y}(t),\mathbf{u}(t)\big)$. The relation between these variables is given by the differential equations

$$\dot{\mathbf{y}}(t) = \mathscr{L}\mathbf{r}_u\big(\mathbf{y}(t),\mathbf{u}(t)\big) + \mathbf{s}_a\big(\mathbf{y}(t),\mathbf{u}(t)\big), \qquad \mathbf{y}(0) = \mathbf{y}_0. \tag{5.1}$$

In the remainder, $\mathbf{r}_u$ and $\mathbf{s}_a$ are written as time-variant signals $\mathbf{r}_u(t)$ and $\mathbf{s}_a(t)$ for the sake of simplicity. However, only the measurements $\tilde{\mathbf{y}}(t)$ and $\tilde{\mathbf{s}}_a(t)$ of $\mathbf{y}(t)$ and $\mathbf{s}_a(t)$, respectively, are available with the sampling period h. Let us define the error variables

$$\begin{cases} \mathbf{d}_{\mathbf{y}}(t) := \tilde{\mathbf{y}}(t) - \mathbf{y}(t) \\ \mathbf{d}_{\mathbf{s}_a}(t) := \tilde{\mathbf{s}}_a(t) - \mathbf{s}_a(t) \end{cases}. \tag{5.2}$$

Furthermore, the measurements $\tilde{\mathbf{y}}(t)$ and $\tilde{\mathbf{s}}_a(t)$ are corrupted by zero-mean noise if and

[1] A variable is considered available if its value can be measured or computed from other measurements.

only if

$$\begin{cases} \mathrm{E}\left[\mathbf{d}_{\mathbf{y}}(t)\right] = \mathbf{0}_{n_y} \\ \mathrm{E}\left[\mathbf{d}_{\mathbf{s}_a}(t)\right] = \mathbf{0}_{n_y} \end{cases} . \tag{5.3}$$

Finally, the measurements $\tilde{\mathbf{y}}(t-mh)$ at different time instants, for $m = 1,\dots,H$, where H is an arbitrary number of sampling times, are independent and identically distributed if and only if [2]

$$\mathrm{Var}\left[\sum_{m=1}^{H} c_m \mathbf{d}_{\mathbf{y}}(t-mh)\right] = \sum_{m=1}^{H} c_m^2 \mathrm{Var}\left[\mathbf{d}_{\mathbf{y}}(t-mh)\right] = \sum_{m=1}^{H} c_m^2 \mathrm{Var}\left[\mathbf{d}_{\mathbf{y}}(t)\right]. \tag{5.4}$$

5.2.1 Transformation to variants

If

$$\mathrm{rank}(\mathscr{L}) = n_r, \tag{5.5}$$

there exists an $n_r \times n_y$ transformation matrix $\mathscr{T}$ such that

$$\mathscr{T}\mathscr{L} = \mathbf{I}_{n_r}. \tag{5.6}$$

Let us assume that the condition in Eq. (5.5) is satisfied. Upon defining the variants

$$\mathbf{y}_r(t) := \mathscr{T}\mathbf{y}(t), \tag{5.7}$$

the application of $\mathscr{T}$ to Eq. (5.1) results in the new dynamic equations

$$\dot{\mathbf{y}}_r(t) = \mathscr{T}\left(\mathscr{L}\mathbf{r}_u(t) + \mathbf{s}_a(t)\right) = \mathbf{r}_u(t) + \mathscr{T}\mathbf{s}_a(t), \qquad \mathbf{y}_r(0) = \mathscr{T}\mathbf{y}_0. \tag{5.8}$$

Then, it becomes clear that $\mathbf{y}_r(t)$, resulting from a linear transformation of the available states $\mathbf{y}(t)$, corresponds to an n_r-dimensional vector of states that are variant with respect to the unknown rates $\mathbf{r}_u(t)$. In fact, each rate variant in $\mathbf{y}_r(t)$ depends on only one unknown rate and contains all the information about that rate. As such, it is decoupled from all the other unknown rates.

The measurements $\tilde{\mathbf{y}}_r(t)$ can be defined as

$$\tilde{\mathbf{y}}_r(t) := \mathscr{T}\tilde{\mathbf{y}}(t) \tag{5.9}$$

[2] Note that the variance of a vector $\mathbf{v}$, denoted as $\mathrm{Var}[\mathbf{v}]$, corresponds to the covariance matrix $\mathrm{Cov}[\mathbf{v},\mathbf{v}]$. Furthermore, the elements on the diagonal of $\mathrm{Var}[\mathbf{v}]$ form the vector $\boldsymbol{\sigma}^2_{\mathbf{v}}$.

and the error variables $\mathbf{d}_{\mathbf{y}_r}(t)$ as

$$\mathbf{d}_{\mathbf{y}_r}(t) := \tilde{\mathbf{y}}_r(t) - \mathbf{y}_r(t). \tag{5.10}$$

To be applicable, the transformation $\mathscr{T}$ requires that at least n_r elements of the vector $\mathbf{y}(t)$ be measured. Note that other transformations could also be used, but they would require stricter rank conditions and thus more measured quantities, and they would be less suitable for data reconciliation in the presence of measurement noise.

The concept of variants presented above allows the estimation of unknown rates without the use of rate models. To see how this is done, let us reformulate Eq. (5.8) for the noisy signals, which yields the estimates of the unknown rates

$$\hat{\mathbf{r}}_u(t) = \dot{\tilde{\mathbf{y}}}_r(t) - \mathscr{T}\,\tilde{\mathbf{s}}_a(t). \tag{5.11}$$

Hence, the estimation of the unknown rates $\mathbf{r}_u(t)$ proceeds via differentiation of the variants $\tilde{\mathbf{y}}_r(t)$ obtained from the measurements $\tilde{\mathbf{y}}(t)$ and uses the knowledge of the quantities $\tilde{\mathbf{s}}_a(t)$.

5.3 Numerical Differentiation Using the Savitzky-Golay Filter

As already mentioned, the unknown rates $\mathbf{r}_u(t)$ can be estimated without the use of a rate model via differentiation of the variants $\tilde{\mathbf{y}}_r(t)$. A differentiation filter with particularly interesting properties, the Savitzky-Golay filter [109], is described in the next proposition.

Proposition 5.1. *Let* $\mathbf{y}$ *be Lipschitz continuous, and let* $\mathscr{D}_q(\tilde{\mathbf{y}}, t)$ *be the differentiation Savitzky-Golay filter of order 1 and odd window size* $q > 1$ *given for the point* q *of the window and applied to the noisy function* $\tilde{\mathbf{y}}$ *on the interval* $[t - \Delta t, t]$*, with* $\Delta t := (q-1)\,h$*. If* $\mathscr{D}_q(\tilde{\mathbf{y}}, t)$ *is defined as*

$$\mathscr{D}_q(\tilde{\mathbf{y}}, t) := \sum_{k=0}^{q-1} \frac{c_{k+1}}{h} \tilde{\mathbf{y}}(t - \Delta t + kh), \tag{5.12}$$

where

$$c_{k+1} = \frac{12\left(k - \frac{q-1}{2}\right)}{q\left(q^2-1\right)}, \qquad k = 0, \ldots, q-1, \tag{5.13}$$

then the expected value of $\mathscr{D}_q(\tilde{\mathbf{y}}, t)$ *is given by*

$$\mathrm{E}\left[\mathscr{D}_q(\tilde{\mathbf{y}}, t)\right] = \mathscr{D}_q(\mathbf{y}, t) = \sum_{k=0}^{q-2} b_{k+1} \int_k^{k+1} \dot{\mathbf{y}}(t - \Delta t + \xi h)\mathrm{d}\xi = \dot{\mathbf{y}}(t) - \mathscr{R}_q(\dot{\mathbf{y}}, t), \tag{5.14}$$

where

$$\mathscr{R}_q(\dot{\mathbf{y}},t)=\sum_{k=0}^{q-2}b_{k+1}\int_k^{k+1}\left(\dot{\mathbf{y}}(t)-\dot{\mathbf{y}}(t-\Delta t+\xi h)\right)\mathrm{d}\xi, \tag{5.15}$$

$$b_{k+1}=\frac{6\left(q-1-k\right)\left(k+1\right)}{q\left(q^2-1\right)}>0,\qquad k=0,\ldots,q-2, \tag{5.16}$$

$$\sum_{k=0}^{q-2}b_{k+1}=1, \tag{5.17}$$

while the covariance of $\sum_{m=1}^{H}\lambda_1^{m-1}h\mathscr{D}_q(\mathbf{d}_\mathbf{y},t-mh)$ *and* $\sum_{m=1}^{H}\lambda_2^{m-1}h\mathscr{D}_q(\mathbf{d}_\mathbf{y},t-mh)$ *and the covariance of* $\sum_{m=1}^{H}\lambda_1^{m-1}h\mathbf{d}_\mathbf{x}(t-mh)$ *and* $\sum_{m=1}^{H}\lambda_2^{m-1}h\mathscr{D}_q(\mathbf{d}_\mathbf{y},t-mh)$*, where* $-1<\lambda_1<1$ *and* $-1<\lambda_2<1$*, are given by*

$$\begin{aligned}&\mathrm{Cov}\left[\sum_{m=1}^{H}\lambda_1^{m-1}h\mathscr{D}_q(\mathbf{d}_\mathbf{y},t-mh),\sum_{m=1}^{H}\lambda_2^{m-1}h\mathscr{D}_q(\mathbf{d}_\mathbf{y},t-mh)\right]\\&=\mathrm{Var}\left[\mathbf{d}_\mathbf{y}(t)\right]\frac{\beta_q(\lambda_1,\lambda_2,H)}{1-\lambda_1\lambda_2},\end{aligned} \tag{5.18}$$

$$\begin{aligned}&\mathrm{Cov}\left[\sum_{m=1}^{H}\lambda_1^{m-1}h\mathbf{d}_\mathbf{x}(t-mh),\sum_{m=1}^{H}\lambda_2^{m-1}h\mathscr{D}_q(\mathbf{d}_\mathbf{y},t-mh)\right]\\&=\mathrm{Cov}\left[\mathbf{d}_\mathbf{x}(t),\mathbf{d}_\mathbf{y}(t)\right]\frac{h\gamma_q(\lambda_1,\lambda_2,H)}{1-\lambda_1\lambda_2},\end{aligned} \tag{5.19}$$

with

$$\begin{aligned}\beta_q(\lambda_1,\lambda_2,H)=&\sum_{l=1}^{\min\left(H,q-1\right)}\left(\lambda_2^l+\lambda_1^l\right)\left(1-\left(\lambda_1\lambda_2\right)^{H-l}\right)\left(\frac{12\left(q-l\right)}{q^2\left(q^2-1\right)}-\frac{24\left(q^2-l^2\right)l}{\left(q\left(q^2-1\right)\right)^2}\right)\\&+\left(1-\left(\lambda_1\lambda_2\right)^H\right)\frac{12}{q\left(q^2-1\right)},\end{aligned} \tag{5.20}$$

$$\gamma_q(\lambda_1,\lambda_2,H)=\sum_{k=\max\left(q-1-H,0\right)}^{q-1}\left(\lambda_1^{-\left(k-q+1\right)}\left(1-\left(\lambda_1\lambda_2\right)^{H+k-q+1}\right)\right)c_{k+1}, \tag{5.21}$$

provided that the measurements $\tilde{\mathbf{y}}(t)$ *are corrupted by zero-mean noise, and the measurements* $\tilde{\mathbf{y}}(t-mh)$ *and* $\tilde{\mathbf{x}}(t-mh)$ *at different time instants, for* $m=1,\ldots,H$*, where* H *is an arbitrary number of sampling times, are independent and identically distributed.*

Furthermore, if q is chosen as

$$q = 1 + 2\max\left\{1, \left\lceil \alpha h^{-\mu} \right\rceil\right\}, \tag{5.22}$$

where $0 < \mu < 1$ and $\alpha > 0$ are adjustable parameters, and

$$\lim_{h\to 0} \frac{\lambda_1 - 1}{h} = -\tau^{-1}, \qquad \lim_{h\to 0} \frac{\lambda_2 - 1}{h} = -\tau^{-1}, \tag{5.23}$$

for some $\tau > 0$, then

$$\lim_{h\to 0} \mathrm{Cov}\left[\sum_{m=1}^{H} \lambda_1^{m-1} h \mathscr{D}_q(\mathbf{d}_\mathbf{y}, t - mh), \sum_{m=1}^{H} \lambda_2^{m-1} h \mathscr{D}_q(\mathbf{d}_\mathbf{y}, t - mh)\right] = \mathbf{0} \tag{5.24}$$

and

$$\lim_{h\to 0} \mathrm{Cov}\left[\sum_{m=1}^{H} \lambda_1^{m-1} h \mathbf{d}_\mathbf{x}(t - mh), \sum_{m=1}^{H} \lambda_2^{m-1} h \mathscr{D}_q(\mathbf{d}_\mathbf{y}, t - mh)\right] = \mathbf{0}. \tag{5.25}$$

Proof. See Appendix D.2. □

5.4 Estimation of Unknown Rates via Numerical Differentiation

The Savitzky-Golay filter presented above is only one alternative among many that can be used to obtain estimates of the unknown rates $\mathbf{r}_u(t)$. However, one can show that, when the unknown rates are constant, this Savitzky-Golay filter corresponds to the *optimal* rate estimator based on convolution filters and on the available states $\mathbf{y}(t)$ and rates $\mathbf{s}_a(t)$. The following subsection shows how this optimal rate estimator based on convolution filters can be constructed, under certain simplifying assumptions.

5.4.1 Rate estimator based on convolution filters

Let us recall that the rate estimates $\hat{\mathbf{r}}_u(t)$ can be computed as shown in Eq. (5.11), which indicates that differentiation needs to be applied to $\tilde{\mathbf{y}}_r$.

A differentiating convolution filter can be used to design a linear rate estimator $\hat{\mathbf{r}}_u(t)$ based on $\tilde{\mathbf{y}}_r(t)$ and $\tilde{\mathbf{s}}_a(t)$ available at the q equally spaced time instants $t - \Delta t, t - \Delta t + h, \ldots, t$ in the time window $[t - \Delta t, t]$, with $\Delta t := (q-1)h$ and h the sampling period. The estimates $\hat{\mathbf{r}}_u(t)$ can be written as:

$$\hat{\mathbf{r}}_u(t) = \sum_{k=0}^{q-1} \frac{c_{k+1}}{h} \tilde{\mathbf{y}}_r(t - \Delta t + kh) - \left(\sum_{k=0}^{q-1} b_{k+1} \mathscr{T}\, \tilde{\mathbf{s}}_a(t - \Delta t + kh)\right), \tag{5.26}$$

where $c_1, \ldots, c_q, b_1, \ldots, b_q$ are adjustable convolution coefficients. Eq. (5.26) indicates that the rate estimates are the result of an FIR (finite impulse response) convolution filter. For analyzing the properties of these estimates, we need to introduce several additional assumptions.

Assumption 5.1. *The unknown rates $\mathbf{r}_u$ are constant in the time window $[t - \Delta t, t]$, which is the case if the states and the inputs that influence these rate expressions are constant.*

Assumption 5.2. *The known rates $\mathbf{s}_a$ are constant between two successive time instants.*

Assumption 5.3. *The quantities $\tilde{\mathbf{y}}_r(t)$ and $\tilde{\mathbf{s}}_a(t)$ are corrupted by zero-mean noise, that is, their expected values are $\mathbf{y}_r(t)$ and $\mathbf{s}_a(t)$.*

Assumption 5.4. *The noise in $\tilde{\mathbf{s}}_a$ is negligible in comparison to the noise in $\tilde{\mathbf{y}}_r$.*

Assumption 5.5. *The noises at different time instants are independent and identically distributed.*

When $\mathbf{r}_u(t)$ is not constant (Assumption 5.1 violated), the estimates $\hat{\mathbf{r}}_u(t)$ will be biased. Appendix D.3 investigates this bias and the variance of $\hat{\mathbf{r}}_u(t)$ when only Assumptions 5.2–5.5 hold. It is shown that the bias depends only on the variations of the unknown rates in the interval $[t - \Delta t, t]$.

For the case of constant $\mathbf{r}_u(t)$, that is, when Assumptions 5.1–5.5 hold, the Savitzky-Golay filter [109] can be used to provide optimal rate estimates with minimal variance, as shown in the next proposition.

Proposition 5.2. *Let Eq.* (5.8) *and Assumptions 5.1–5.5 hold. Then, the rate estimator that provides minimal variance among all unbiased rate estimators is given by Eq.* (5.26) *with*

$$c_{k+1}^* = \frac{12\left(k - \frac{q-1}{2}\right)}{q\left(q^2-1\right)}, \qquad \forall k = 0, \ldots, q-1, \tag{5.27}$$

$$b_{k+1}^* = \frac{6\left(q-k-1\right)\left(k+1\right)}{q\left(q^2-1\right)}, \qquad \forall k = 0, \ldots, q-1, \tag{5.28}$$

where the optimal coefficients $c_1^*, \ldots, c_q^*$ correspond to the coefficients of the differentiation Savitzky-Golay filter of order 1 and window size q. Moreover, the variance is given by

$$\mathrm{Var}\left[\hat{\mathbf{r}}_u(t)\right] = \frac{12}{q\left(q^2-1\right)} \frac{\mathrm{Var}\left[\tilde{\mathbf{y}}_r(t)\right]}{h^2}. \tag{5.29}$$

Proof. A sketch of the proof is given next. The complete proof can be found in Appendix D.4.

Since (i) any Savitzky-Golay filter is based on the local fit of a polynomial of a certain order to the discrete signal $\tilde{\mathbf{y}}_r$, and (ii) $\mathbf{r}_u$ is locally constant, the filter that provides minimal variance is the Savitzky-Golay filter of lowest order that can yield the first derivative of $\tilde{\mathbf{y}}_r$, in this case of order 1. □

Note that the rate estimator given in Proposition 5.2 can also be used to estimate $\hat{\mathbf{r}}_u(t)$ when $\mathbf{r}_u(t)$ is not constant. In this case, however, it is no longer possible to guarantee unbiased estimation with this estimator or any other, because no information about the true rates $\mathbf{r}_u(t)$ is available.

Remark 5.1. Instead of using a differentiating convolution filter, one could also design an observer for rate estimation. Since it is assumed in this chapter that the rate model is unknown, the use of model-based observers is excluded. However, one could still use an observer that considers the known part of the dynamics in Eq. (5.8) to estimate the values $\mathbf{r}_u(t)$ of the unknown rates [2, 110]. Owing to the linear structure of Eq. (5.8), this observer would be linear, that is, represented by a linear system with inputs $\tilde{\mathbf{y}}_r(t)$ and $\tilde{\mathbf{s}}_a(t)$ and outputs $\hat{\mathbf{r}}_u(t)$. Then, for any order of the linear observer, it would be equivalent to an IIR (infinite impulse response) convolution filter. However, for any BIBO (bounded-input bounded-output) stable IIR convolution filter, the impulse response tends to zero after some time, which means that any linear observer would essentially be equivalent to an FIR convolution filter with a sufficiently large window size. Since Proposition 5.2 provides the optimal rate estimator that uses an FIR convolution filter with a given window size, an observer would not yield better results.

5.4.2 Maximum-likelihood estimation of unknown rates

Different transformation matrices $\mathscr{T}$ that satisfy the condition in Eq. (5.6) can be found. An example is the Moore-Penrose pseudoinverse of the matrix $\mathscr{L}$. However, when only noisy measurements are available, a better alternative is to consider an estimator of the unknown rates $\mathbf{r}_u(t)$ in the maximum-likelihood sense. The text below describes such a method to compute $\mathscr{T}$, using prior knowledge about the variance of the noisy measurements.

As shown in Proposition 5.1, if $\mathbf{y}$ is Lipschitz continuous,

$$\begin{aligned}
\mathscr{D}_q(\mathbf{y},t) &= \sum_{k=0}^{q-2} b_{k+1} \int_k^{k+1} \dot{\mathbf{y}}(t-\Delta t+\xi h)\mathrm{d}\xi \\
&= \sum_{k=0}^{q-2} b_{k+1} \int_k^{k+1} \left(\mathscr{L}\mathbf{r}_u(t-\Delta t+\xi h)+\mathbf{s}_a(t-\Delta t+\xi h)\right)\mathrm{d}\xi \\
&= \sum_{k=0}^{q-2} b_{k+1} \int_k^{k+1} \mathscr{L}\mathbf{r}_u(t-\Delta t+\xi h)\mathrm{d}\xi + \sum_{k=0}^{q-2} b_{k+1} \int_k^{k+1} \mathbf{s}_a(t-\Delta t+kh)\mathrm{d}\xi \\
&= \mathscr{L}\left(\mathbf{r}_u(t)-\mathscr{R}_q(\mathbf{r}_u,t)\right) + \sum_{k=0}^{q-2} b_{k+1}\mathbf{s}_a(t-\Delta t+kh),
\end{aligned} \tag{5.30}$$

since

$$\mathbf{s}_a(t-\Delta t+\xi h) = \mathbf{s}_a(t-\Delta t+kh), \tag{5.31}$$

for all $k = 0,\ldots,q-2$ and for all $\xi \in [k,k+1)$, if Assumption 5.2 holds.

Let us define $\mathbf{y}^{UV}(t)$, the unknown-variant form (UV) of $\mathbf{y}(t)$, with the differential equation

$$\dot{\mathbf{y}}^{UV}(t) = \mathscr{L}\left(\mathbf{r}_u(t) - \mathscr{R}_q(\mathbf{r}_u, t)\right), \qquad \mathbf{y}^{UV}(0) = \mathbf{0}_{n_y}, \tag{5.32}$$

and the weighted sum of past values of $\tilde{\mathbf{s}}_a$ as

$$\mathscr{W}_q(\tilde{\mathbf{s}}_a, t) := \sum_{k=0}^{q-2} b_{k+1}\tilde{\mathbf{s}}_a(t - \Delta t + kh), \tag{5.33}$$

whose expected value, assuming that the measurements $\tilde{\mathbf{s}}_a(t)$ are corrupted by zero-mean noise as stated in Assumption 5.3, is

$$\mathrm{E}\left[\mathscr{W}_q(\tilde{\mathbf{s}}_a, t)\right] = \mathscr{W}_q(\mathbf{s}_a, t) = \sum_{k=0}^{q-2} b_{k+1}\mathbf{s}_a(t - \Delta t + kh). \tag{5.34}$$

Then, Eq. (5.30) can be reformulated as

$$\dot{\mathbf{y}}^{UV}(t) = \mathscr{D}_q(\mathbf{y}, t) - \mathscr{W}_q(\mathbf{s}_a, t). \tag{5.35}$$

This leads to the definition of the approximation of $\dot{\mathbf{y}}^{UV}(t)$, which uses measured quantities as follows:

$$\tilde{\dot{\mathbf{y}}}^{UV}(t) = \mathscr{D}_q(\tilde{\mathbf{y}}, t) - \mathscr{W}_q(\tilde{\mathbf{s}}_a, t). \tag{5.36}$$

The difference between the real value and the approximation of $\dot{\mathbf{y}}^{UV}(t)$ is given by

$$\begin{aligned}\tilde{\dot{\mathbf{y}}}^{UV}(t) - \dot{\mathbf{y}}^{UV}(t) &= \mathscr{D}_q(\tilde{\mathbf{y}}, t) - \mathscr{W}_q(\tilde{\mathbf{s}}_a, t) - \mathscr{D}_q(\mathbf{y}, t) + \mathscr{W}_q(\mathbf{s}_a, t) \\ &= \mathscr{D}_q(\mathbf{d}_\mathbf{y}, t),\end{aligned} \tag{5.37}$$

if the noise in $\tilde{\mathbf{s}}_a$ is negligible in comparison to the noise in $\tilde{\mathbf{y}}_r$, that is, if Assumption 5.4 holds.

This implies that

$$\mathrm{E}\left[\tilde{\dot{\mathbf{y}}}^{UV}(t) - \dot{\mathbf{y}}^{UV}(t)\right] = \mathbf{0}_{n_y}, \tag{5.38}$$

if $\tilde{\mathbf{y}}$ is corrupted by zero-mean noise, which is similar to Assumption 5.3.

Furthermore, if one defines

$$\mathbf{\Sigma}_{\dot{\mathbf{y}}} := \mathrm{Var}\left[\tilde{\dot{\mathbf{y}}}^{UV}(t) - \dot{\mathbf{y}}^{UV}(t)\right] \tag{5.39}$$

and assumes that the measurements $\tilde{\mathbf{y}}(t - mh)$ at different time instants, for $m = 1, \ldots, H$, where H is an arbitrary number of sampling times, are independent and identically dis-

tributed, which is similar to Assumption 5.5, then

$$\begin{aligned}\boldsymbol{\Sigma}_{\dot{\mathbf{y}}} &= \mathrm{Var}\left[\mathscr{D}_q(\mathbf{d}_\mathbf{y}, t)\right] \\ &= \frac{\mathrm{Var}\left[\mathbf{d}_\mathbf{y}(t)\right]}{h^2}\beta_q(0,0,H) \\ &= \frac{\mathrm{Var}\left[\mathbf{d}_\mathbf{y}(t)\right]}{h^2}\frac{12}{q\left(q^2-1\right)}.\end{aligned} \tag{5.40}$$

Hence, if one assumes that

$$\tilde{\dot{\mathbf{y}}}^{UV}(t) - \dot{\mathbf{y}}^{UV}(t) \sim \mathcal{N}(\mathbf{0}_{n_y}, \boldsymbol{\Sigma}_{\dot{\mathbf{y}}}), \tag{5.41}$$

where $\mathcal{N}(\boldsymbol{\mu}, \boldsymbol{\Sigma})$ denotes the normal distribution with mean $\boldsymbol{\mu}$ and variance-covariance $\boldsymbol{\Sigma}$, then Eqs. (5.32) and (5.36) imply that $\hat{\mathbf{r}}_u(t)$, the maximum likelihood estimator of $\mathbf{r}_u(t) - \mathscr{R}_q(\mathbf{r}_u, t)$, corresponds to the minimization of the weighted least squares problem

$$\min_{\hat{\mathbf{r}}_u(t)} \left(\tilde{\dot{\mathbf{y}}}^{UV}(t) - \mathscr{L}\hat{\mathbf{r}}_u(t)\right)^{\mathrm{T}} \boldsymbol{\Sigma}_{\dot{\mathbf{y}}}^{-1} \left(\tilde{\dot{\mathbf{y}}}^{UV}(t) - \mathscr{L}\hat{\mathbf{r}}_u(t)\right) \tag{5.42}$$

and is given by

$$\hat{\mathbf{r}}_u(t) = \mathscr{T}\tilde{\dot{\mathbf{y}}}^{UV}(t) = \mathscr{D}_q(\tilde{\mathbf{y}}_r, t) - \mathscr{T}\mathscr{W}_q(\tilde{\mathbf{s}}_a, t), \tag{5.43}$$

where

$$\mathscr{T} = \left(\mathscr{L}^{\mathrm{T}}\boldsymbol{\Sigma}_{\dot{\mathbf{y}}}^{-1}\mathscr{L}\right)^{-1}\mathscr{L}^{\mathrm{T}}\boldsymbol{\Sigma}_{\dot{\mathbf{y}}}^{-1}, \tag{5.44}$$

which satisfies Eq. (5.6), and $\tilde{\mathbf{y}}_r(t)$ are defined as in Eq. (5.9), using $\mathscr{T}$ from Eq. (5.44).

According to Eq. (5.43), the estimation of the unknown rates $\mathbf{r}_u(t)$ proceeds via application of a differentiation filter to the variants $\mathbf{y}_r(t)$ that are obtained via transformation of the available state vector $\mathbf{y}(t)$, and the knowledge of the previous values of the available rates $\mathbf{s}_a(t)$. Note that Eq. (5.43) can be obtained from Eq. (5.8) if one replaces $\mathbf{r}_u(t)$ by $\hat{\mathbf{r}}_u(t)$, $\dot{\mathbf{y}}_r(t)$ by $\mathscr{D}_q(\tilde{\mathbf{y}}_r, t)$, and $\mathbf{s}_a(t)$ by $\mathscr{W}_q(\tilde{\mathbf{s}}_a, t)$.

5.4.3 Error of the estimates of unknown rates

The next proposition shows the final result of this section, which concerns the error and variance of the estimates of the unknown rates $\mathbf{r}_u(t)$.

Proposition 5.3. *Let the condition in Eq.* (5.5) *be satisfied, the transformation matrix* $\mathscr{T}$ *be given by Eq.* (5.44)*,* $\tilde{\mathbf{y}}_r(t)$ *be defined as in Eq.* (5.9)*,* $\mathscr{D}_q(\tilde{\mathbf{y}}_r, t)$ *be defined as in Eq.* (5.12)*,* $\mathscr{W}_q(\tilde{\mathbf{s}}_a, t)$ *be defined as in Eq.* (5.33)*, and* $\hat{\mathbf{r}}_u(t)$ *be defined as in Eq.* (5.43)*. Then,*

$$\hat{\mathbf{r}}_u(t) - \mathbf{r}_u(t) = -\mathscr{R}_q(\mathbf{r}_u, t) + \mathscr{T}\mathscr{D}_q(\mathbf{d}_\mathbf{y}, t), \tag{5.45}$$

and

$$\text{Var}\left[\hat{\mathbf{r}}_u(t)\right] = \mathscr{T}\boldsymbol{\Sigma}_{\dot{\mathbf{y}}}\mathscr{T}^{\mathrm{T}} = \left(\mathscr{L}^{\mathrm{T}}\boldsymbol{\Sigma}_{\dot{\mathbf{y}}}^{-1}\mathscr{L}\right)^{-1}. \tag{5.46}$$

Proof. One has to simply notice that, from Eqs. (5.32), (5.37), (5.43), and (5.44),

$$\begin{aligned}\hat{\mathbf{r}}_u(t) - \mathbf{r}_u(t) &= \hat{\mathbf{r}}_u(t) - \mathscr{T}\mathscr{L}\mathbf{r}_u(t)\\ &= \mathscr{T}\left(\tilde{\dot{\mathbf{y}}}^{UV}(t) - \dot{\mathbf{y}}^{UV}(t)\right) - \mathscr{T}\mathscr{L}\mathscr{R}_q(\mathbf{r}_u, t)\\ &= -\mathscr{R}_q(\mathbf{r}_u, t) + \mathscr{T}\mathscr{D}_q(\mathbf{d}_{\mathbf{y}}, t)\end{aligned} \tag{5.47}$$

and

$$\text{Var}\left[\hat{\mathbf{r}}_u(t)\right] = \mathscr{T}\text{Var}\left[\tilde{\dot{\mathbf{y}}}^{UV}(t)\right]\mathscr{T}^{\mathrm{T}} = \mathscr{T}\boldsymbol{\Sigma}_{\dot{\mathbf{y}}}\mathscr{T}^{\mathrm{T}} = \left(\mathscr{L}^{\mathrm{T}}\boldsymbol{\Sigma}_{\dot{\mathbf{y}}}^{-1}\mathscr{L}\right)^{-1}. \tag{5.48}$$

□

5.5 Conclusion

This chapter has shown how to compute the unknown rates $\mathbf{r}_u(t)$ from the available measurements, using knowledge about the structural relationship, given by the matrix $\mathscr{L}$, between the available states $\mathbf{y}(t)$ on the one hand and the unknown rates $\mathbf{r}_u(t)$ and the available rates $\mathbf{s}_a(t)$ on the other hand. The variants $\mathbf{y}_r(t)$ are variant with respect to the unknown rates $\mathbf{r}_u(t)$. The unknown rates $\mathbf{r}_u(t)$ are estimated via numerical differentiation of the variants $\mathbf{y}_r(t)$ that are computed from the available states $\mathbf{y}(t)$ via an appropriate linear transformation, without the use of any rate model. For this, the rank of $\mathscr{L}$ must be equal to the number of estimated unknown rates n_r, which implies that the number of states that are available has to be greater than or equal to n_r. Only one parameter needs to be tuned, namely, the parameter of the differentiation filter (the number of samples q in the case of the Savitzky-Golay filter) used for numerical differentiation of variants $\mathbf{y}_r(t)$.

The implications of this estimation of rate signals without kinetic models for monitoring and diagnosis are obvious. Furthermore, the next two chapters present the implications of rate estimation with respect to control without kinetic models and estimation of plant steady state, which can then be used for real-time optimization.

6 Reactor Control

Part of this chapter is adapted from the postprint of the following article [111]:

D. Rodrigues, J. Billeter, and D. Bonvin. Control of reaction systems via rate estimation and feedback linearization. *Comput. Aided Chem. Eng.*, 37:137–142, 2015.

Link: http://doi.org/10.1016/B978-0-444-63578-5.50018-9.

The author of this thesis contributed to that article by developing the main novel ideas, implementing the simulations, and writing a significant part of the text. Hence, the author retains the right to include the article in this thesis since it is not published commercially and the journal is referenced as the original source.

6.1 Introduction

Various control structures for homogeneous reactors based on reaction variants, extensive variables, and inventories have been proposed throughout the years. For example, Hammarström [28] claimed that the control of reaction and control variants in homogeneous reactors is useful to reduce the number of controlled and measured variables. Georgakis [112] was among the first to suggest the use of extensive variables for efficient design of multivariable and nonlinear controllers for process units, namely reactors. Farschman et al. [113] proposed a structure called inventory control, whereby a certain type of extensive variables called inventories are controlled efficiently via input-output feedback linearization, although the proposed structure implies the use of a kinetic model for estimation of reaction rates in the case of reactor control. Aggarwal et al. [41] expressed the model of multi-phase reaction systems operating at thermodynamic equilibrium in terms of reaction invariants and used this formulation for inventory control of these invariant quantities, labeled as invariant inventories. Hoang et al. [31] proposed to use the fact that the reaction invariants are exponentially stable to control only the reaction variants, although at the price of requiring the use of a kinetic model to compute the reaction rates. In an earlier and more restricted version of the developments presented in this chapter and also in the pre-

vious one, Rodrigues et al. [111] proposed temperature control in homogeneous reactors without the use of kinetic models, which was enabled by the estimation of the unknown reaction rates via numerical differentiation. Then, Zhao et al. [32] took advantage of this possibility to propose another scheme for control of reaction variants, but this time without the use of kinetic models since the reaction rates can be estimated from measurements without a kinetic model. However, there does not exist a systematic way of taking advantage of multiple measurements of variables that are not directly controlled to simplify the design of multiple-input multiple-output (MIMO) control of the temperature and concentrations (or their extensive counterparts, the heat and numbers of moles) in homogeneous reactors, in particular without the use of a kinetic model. The development of such systematic procedures is the main objective of this chapter.

This chapter starts by presenting in Section 6.2 a control approach that uses the kinetic model to achieve offset-free control of as many controlled variables as the number of manipulated variables and to set the closed-loop time constants of all the variables that represent the reaction system. Then, a feedback linearization approach that is based on the estimation of unknown rates using the concept of variants is presented in Section 6.3, thus allowing effective control without the use of rate models for these unknown rates. In particular, the possibility of controlling homogeneous reactors without the use of kinetic models is investigated. The reaction rates are estimated without the use of kinetic models and then used via a feedback-linearization scheme to control the reactor temperature and reactant concentrations by manipulating the amount of heat that is exchanged with the environment and the inlet flowrates in a homogeneous reactor. Finally, Section 6.4 concludes the chapter.

6.2 Control with Kinetic Models

6.2.1 System description

As shown in Section 2.5, the S-dimensional vector of numbers of moles $\mathbf{n}(t)$ in a homogeneous reaction system with R independent reactions and p independent inlets can be obtained from the linear transformation of vessel extents

$$\mathbf{n}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{x}_r(t) + \mathbf{W}_{in}\mathbf{x}_{in}(t) + \mathbf{n}_0 x_{ic}(t), \tag{6.1}$$

where $\mathbf{N}$ is the $R \times S$ stoichiometric matrix, $\mathbf{W}_{in}$ is the $S \times p$ inlet-composition matrix, $\mathbf{n}_0$ is the S-dimensional vector of initial numbers of moles, $\mathbf{x}_r(t)$ is the R-dimensional vector of vessel extents of reaction, $\mathbf{x}_{in}(t)$ is the p-dimensional vector of vessel extents of inlet, and $x_{ic}(t)$ is the vessel extent of initial conditions. For the sake of simplicity, the developments in this section deal only with the case of a constant x_{ic}. For example, (i) $x_{ic} = 1$ in reactors without outlet, and (ii) $x_{ic} = 0$ in reactors with outlet once the effect of the initial conditions is removed.[1] Moreover, the mass m can be obtained from the linear combination of the

[1] In practice, this is the case after 5 residence times. For example, this can be ensured by flushing the reactor with one or several inlets until this condition is satisfied.

numbers of moles

$$m(t) = \mathbf{1}_S^{\mathrm{T}} \mathbf{M}_w \mathbf{n}(t), \tag{6.2}$$

where $\mathbf{M}_w$ is the S-dimensional diagonal matrix of molecular weights.

According to Eqs. (6.1) and (6.2), it is possible to obtain all the variables $\mathbf{n}(t)$ and $m(t)$ from the $R+p$ vessel extents of reaction and inlet. These vessel extents $\mathbf{x}_v(t) := \begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{in}(t) \end{bmatrix}$ are described by the differential equations

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t), \qquad \mathbf{x}_r(0) = \mathbf{0}_R, \tag{6.3a}$$

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) - \omega(t)\mathbf{x}_{in}(t), \qquad \mathbf{x}_{in}(0) = \mathbf{0}_p, \tag{6.3b}$$

where $\mathbf{u}_{in}(t)$ is the p-dimensional vector of inlet flowrates, $\omega(t)$ is the inverse of the residence time, and

$$\mathbf{r}_v(t) := \upsilon\big(\mathbf{n}(t)\big)\boldsymbol{\varphi}\big(\mathbf{n}(t)\big), \tag{6.4}$$

with $\upsilon(\mathbf{n})$ the volume and $\boldsymbol{\varphi}(\mathbf{n})$ the R-dimensional vector of reaction rates expressed as a function of the numbers of moles.

It is also possible to obtain all the variables $\mathbf{n}(t)$ and $m(t)$ from only $R+p$ numbers of moles $\mathbf{n}_a(t)$. To show this, note that

$$\mathbf{n}_a(t) = \mathbf{N}_a^{\mathrm{T}} \mathbf{x}_r(t) + \mathbf{W}_{in,a} \mathbf{x}_{in}(t) + \mathbf{n}_{a,0} x_{ic}, \tag{6.5}$$

which implies that one can solve Eq. (6.5) for the vessel extents $\mathbf{x}_v(t)$ and reconstruct the numbers of moles $\mathbf{n}(t)$ from Eq. (6.1). This results in

$$\mathbf{n}(t) = \mathscr{L}\mathscr{T}_a \left(\mathbf{n}_a(t) - \mathbf{n}_{a,0} x_{ic}\right) + \mathbf{n}_0 x_{ic}, \tag{6.6}$$

where $\mathscr{T}_a := \begin{bmatrix} \mathbf{N}_a^{\mathrm{T}} & \mathbf{W}_{in,a} \end{bmatrix}^{-1}$ and $\mathscr{L} := \begin{bmatrix} \mathbf{N}^{\mathrm{T}} & \mathbf{W}_{in} \end{bmatrix}$.

Hence, to control all the variables in the system, one needs to consider only $\mathbf{x}_v(t)$ or $\mathbf{n}_a(t)$ as controlled variables. The manipulated variables are $\mathbf{u}_{in}(t)$ and possibly $\omega(t)$. In the case of the control of $\mathbf{x}_v(t)$, note that the R vessel extents of reaction $\mathbf{x}_r(t)$ typically have relative degree two with respect to $\mathbf{u}_{in}(t)$, while the p vessel extents of inlet $\mathbf{x}_{in}(t)$ have relative degree one with respect to $\mathbf{u}_{in}(t)$. As shown in the sequel, it is also helpful to keep this feature when the control of $\mathbf{n}_a(t)$ is considered.

For this reason, it is assumed that R numbers of moles $\mathbf{n}_a(t)$ have relative degree two with respect to $\mathbf{u}_{in}(t)$ and are denoted $\mathbf{n}_t(t)$, and the remaining p numbers of moles $\mathbf{n}_a(t)$ have relative degree one with respect to $\mathbf{u}_{in}(t)$ and are denoted $\mathbf{n}_o(t)$, which is typically true if the p inlets contain p species. These numbers of moles $\mathbf{n}_a(t) := \begin{bmatrix} \mathbf{n}_t(t) \\ \mathbf{n}_o(t) \end{bmatrix}$ are described

by the differential equations

$$\dot{\mathbf{n}}_t(t) = \boldsymbol{\phi}^{\nu}_{r,t}(t) - \omega(t)\mathbf{n}_t(t), \qquad \mathbf{n}_t(0) = \mathbf{n}_{t,0}, \tag{6.7a}$$

$$\dot{\mathbf{n}}_o(t) = \mathbf{N}_o^{\mathrm{T}}\mathbf{r}_{\nu}(t) + \mathbf{W}_{in,o}\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}_o(t), \qquad \mathbf{n}_o(0) = \mathbf{n}_{o,0}, \tag{6.7b}$$

where

$$\boldsymbol{\phi}^{\nu}_{r,t}(t) := \mathbf{N}_t^{\mathrm{T}}\upsilon\big(\mathbf{n}(t)\big)\varphi\big(\mathbf{n}(t)\big). \tag{6.8}$$

Then, one can replace $\mathbf{n}_t(t)$ and $\mathbf{n}_o(t)$ in Eq. (6.6). This results in

$$\mathbf{n}(t) = \mathscr{L}\mathscr{T}_t\left(\mathbf{n}_t(t) - \mathbf{n}_{t,0}x_{ic}\right) + \mathscr{L}\mathscr{T}_o\left(\mathbf{n}_o(t) - \mathbf{n}_{o,0}x_{ic}\right) + \mathbf{n}_0 x_{ic}, \tag{6.9}$$

where $\mathscr{T}_a = \begin{bmatrix}\mathscr{T}_t & \mathscr{T}_o\end{bmatrix}$, with $\mathscr{T}_t$ of dimension $(R+p)\times R$ and $\mathscr{T}_o$ of dimension $(R+p)\times p$.

Let n_u denote the number of manipulated variables. Two cases can be considered: (i) if only the inlet flowrates $\mathbf{u}_{in}(t)$ are manipulated and $\omega(t)$ is known in advance (which is always the case in reactors without outlet), then $n_u = p$; (ii) if $\omega(t)$ is also manipulated as part of the control scheme, then $n_u = p+1$. In both cases, one would like to set the closed-loop time constants of all the variables, while obtaining offset-free control of n_u variables.

Section 6.2.2 details how one can use feedback linearization and linear feedback control to set the closed-loop time constants of all the variables, while obtaining offset-free control of the mass and $n_u - 1$ vessel extents, with emphasis on the case $n_u = p$. Section 6.2.3 obtains similar results, but with offset-free control of the mass and $n_u - 1$ numbers of moles. Section 6.2.4 illustrates the performance of this control scheme via a simulated example.

Complete knowledge of the dynamic model and perfect measurements of $R+p$ states (either $\mathbf{x}_v(t)$ or $\mathbf{n}_a(t)$) are assumed to prove these results. However, the plant-model mismatch and the bias caused by measurement errors are typically significant in reaction systems. These deviations from the ideal case can be treated as disturbances to the linear system that is obtained with feedback linearization. Then, one can still specify bounds for these disturbances and design robust linear feedback controllers to ensure similar results in the presence of these disturbances.

6.2.2 Offset-free control of vessel extents

Let us assume that we would like to obtain offset-free control of the mass and $n_u - 1$ vessel extents, where R of these vessel extents are $\mathbf{x}_r$, and the remaining $n_u - 1 - R$ vessel extents are part of $\mathbf{x}_{in}$ and are denoted $\mathbf{x}_{in,c}$, which implies that $n_u - 1 \geq R$.[2] Let us define

[2]The vessel extents of inlet are partitioned as $\mathbf{x}_{in}(t) = \begin{bmatrix}\mathbf{x}_{in,n}(t)\\ \mathbf{x}_{in,c}(t)\end{bmatrix}$, with $\mathbf{x}_{in,n} = \mathbf{S}_{x,n}\mathbf{x}_{in}$ of dimension $p - (n_u - 1) + R$ and $\mathbf{x}_{in,c} = \mathbf{S}_{x,c}\mathbf{x}_{in}$ of dimension $n_u - 1 - R$. If the mass m is not controlled, offset-free control of n_u vessel extents (instead of $n_u - 1$) can be obtained, and all the occurences of $n_u - 1$ in this section are changed to n_u, but no guarantee can be given regarding the dimension of the system.

$\mathbf{s}_r$ as the right-hand side of Eq. (6.3a), that is,

$$\mathbf{s}_r(t) := \mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t). \tag{6.10}$$

One would like to manipulate the p flowrates $\mathbf{u}_{in}$ (and possibly the inverse of the residence time ω) to implement feedback linearization, such that the R vessel extents $\mathbf{x}_r$, the R rates $\mathbf{s}_r$, the mass m and the $n_u - 1 - R$ vessel extents $\mathbf{x}_{in,c}$ obey the dynamics

$$\dot{\mathbf{x}}_r(t) = \mathbf{s}_r(t), \tag{6.11a}$$
$$\dot{\mathbf{s}}_r(t) = \mathbf{v}_r(t), \tag{6.11b}$$
$$\dot{m}(t) = v_m(t), \tag{6.11c}$$
$$\dot{\mathbf{x}}_{in,c}(t) = \mathbf{v}_{in,c}(t), \tag{6.11d}$$

where $\mathbf{v}_r(t)$, $v_m(t)$, and $\mathbf{v}_{in,c}(t)$ are new inputs. That is, one would like to obtain

$$\dot{\mathbf{z}}_x(t) = \mathbf{A}\mathbf{z}_x(t) + \mathbf{B}\mathbf{v}_x(t), \tag{6.12}$$

with the $(R + n_u)$-dimensional vector of new states

$$\mathbf{z}_x(t) := \begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{s}_r(t) \\ m(t) \\ \mathbf{x}_{in,c}(t) \end{bmatrix}, \tag{6.13}$$

the n_u-dimensional vector of new inputs

$$\mathbf{v}_x(t) := \begin{bmatrix} \mathbf{v}_r(t) \\ v_m(t) \\ \mathbf{v}_{in,c}(t) \end{bmatrix}, \tag{6.14}$$

the $(R + n_u) \times (R + n_u)$ state matrix

$$\mathbf{A} := \begin{bmatrix} \mathbf{0}_{R\times R} & \mathbf{I}_R & \mathbf{0}_R & \mathbf{0}_{R\times(n_u-1-R)} \\ \mathbf{0}_{R\times R} & \mathbf{0}_{R\times R} & \mathbf{0}_R & \mathbf{0}_{R\times(n_u-1-R)} \\ \mathbf{0}_R^{\mathrm{T}} & \mathbf{0}_R^{\mathrm{T}} & 0 & \mathbf{0}_{n_u-1-R}^{\mathrm{T}} \\ \mathbf{0}_{(n_u-1-R)\times R} & \mathbf{0}_{(n_u-1-R)\times R} & \mathbf{0}_{n_u-1-R} & \mathbf{0}_{(n_u-1-R)\times(n_u-1-R)} \end{bmatrix}, \tag{6.15}$$

and the $(R + n_u) \times n_u$ input matrix

$$\mathbf{B} := \begin{bmatrix} \mathbf{0}_{R\times R} & \mathbf{0}_R & \mathbf{0}_{R\times(n_u-1-R)} \\ \mathbf{I}_R & \mathbf{0}_R & \mathbf{0}_{R\times(n_u-1-R)} \\ \mathbf{0}_R^{\mathrm{T}} & 1 & \mathbf{0}_{n_u-1-R}^{\mathrm{T}} \\ \mathbf{0}_{(n_u-1-R)\times R} & \mathbf{0}_{n_u-1-R} & \mathbf{I}_{n_u-1-R} \end{bmatrix}, \tag{6.16}$$

which implies that the linear system specified by $\mathbf{A}$ and $\mathbf{B}$ is controllable.

Note that it is possible to compute $\mathbf{z}_x(t)$ from the knowledge of $\mathbf{x}_v(t)$ and $\omega(t)$ if one notes that $\mathbf{x}_r(t)$ and $\mathbf{x}_{in,c}(t)$ are part of $\mathbf{x}_v(t)$ and one uses Eqs. (6.4) and (6.10) for $\mathbf{s}_r(t)$ and Eq. (6.2) for $m(t)$, with $\mathbf{n}(t)$ given by Eq. (6.1). Furthermore, since

$$\begin{aligned}\dot{\mathbf{s}}_r(t) &= \frac{\partial \mathbf{r}_v(t)}{\partial \mathbf{n}}\dot{\mathbf{n}}(t) - \omega(t)\dot{\mathbf{x}}_r(t) - \dot{\omega}(t)\mathbf{x}_r(t) \\ &= \frac{\partial \mathbf{r}_v(t)}{\partial \mathbf{n}}\left(\mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}(t)\right) - \omega(t)\left(\mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t)\right) \\ &\quad - \dot{\omega}(t)\mathbf{x}_r(t), \end{aligned} \tag{6.17}$$

$$\begin{aligned}\dot{m}(t) &= \mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\left(\mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}(t)\right) \\ &= \mathbf{1}_p^{\mathrm{T}}\mathbf{u}_{in}(t) - \omega(t)m(t), \end{aligned} \tag{6.18}$$

the change of variables $\mathbf{z}_x(t) = \mathbf{t}_x\left(\mathbf{x}_v(t)\right)$ transforms Eqs. (6.3a)-(6.3b) into the form

$$\dot{\mathbf{z}}_x(t) = \mathbf{A}\mathbf{z}_x(t) + \mathbf{B}\Big(\mathbf{Q}_x\left(\mathbf{x}_v(t)\right)\mathbf{u}_{in}(t) + \mathbf{p}_x\left(\mathbf{x}_v(t)\right)\Big), \tag{6.19}$$

with

$$\mathbf{Q}_x\left(\mathbf{x}_v(t)\right) := \begin{bmatrix} \frac{\partial \mathbf{r}_v(t)}{\partial \mathbf{n}}\mathbf{W}_{in} \\ \mathbf{1}_p^{\mathrm{T}} \\ \mathbf{S}_{x,c} \end{bmatrix}, \tag{6.20a}$$

$$\begin{aligned}\mathbf{p}_x\left(\mathbf{x}_v(t)\right) := &\begin{bmatrix} \frac{\partial \mathbf{r}_v(t)}{\partial \mathbf{n}}\mathbf{N}^{\mathrm{T}} \\ \mathbf{0}_R^{\mathrm{T}} \\ \mathbf{0}_{(n_u-1-R)\times R} \end{bmatrix}\mathbf{r}_v(t) - \omega(t)\begin{bmatrix} \frac{\partial \mathbf{r}_v(t)}{\partial \mathbf{n}}\mathbf{n}(t) + \mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t) \\ m(t) \\ \mathbf{x}_{in,c}(t) \end{bmatrix} \\ &- \dot{\omega}(t)\begin{bmatrix} \mathbf{x}_r(t) \\ 0 \\ \mathbf{0}_{n_u-1-R} \end{bmatrix}, \end{aligned} \tag{6.20b}$$

if $\omega(t)$ and its derivative $\dot{\omega}(t)$ are known in advance ($n_u = p$).

Then, the feedback linearization law that achieves the desired linearized dynamics is

$$\mathbf{u}_{in}(t) = \mathbf{Q}_x\left(\mathbf{x}_v(t)\right)^{-1}\Big(\mathbf{v}_x(t) - \mathbf{p}_x\left(\mathbf{x}_v(t)\right)\Big), \tag{6.21}$$

if $n_u = p$.[3]

Eq. (6.11) corresponds to a controllable linear system, where the states are the R vessel extents $\mathbf{x}_r$, the R rates $\mathbf{s}_r$, the mass m and the $n_u - 1 - R$ vessel extents $\mathbf{x}_{in,c}$. Then, it is possible to set the closed-loop time constants of these $R + n_u$ variables and to obtain offset-

[3] If $\omega(t)$ and its derivative $\dot{\omega}(t)$ are also manipulated as part of the control scheme ($n_u = p + 1$), then $\omega(t)$ becomes an additional state of the system, and Eqs. (6.19)–(6.21) are formulated in terms of the manipulated variables $\begin{bmatrix} \mathbf{u}_{in}(t) \\ \dot{\omega}(t) \end{bmatrix}$ instead of $\mathbf{u}_{in}(t)$. Hence, all the results in this section also hold for the case $n_u = p + 1$.

free control of the n_u variables $\mathbf{x}_r(t)$, $m(t)$ and $\mathbf{x}_{in,c}(t)$ to the setpoints $\mathbf{x}_r^s(t)$, $m^s(t)$ and $\mathbf{x}_{in,c}^s(t)$ by choosing the feedback control laws

$$\mathbf{v}_r(t) = \ddot{\mathbf{x}}_r^s(t) + 2\mathbf{K}_r\left(\dot{\mathbf{x}}_r^s(t) - \mathbf{r}_v(t) + \omega(t)\mathbf{x}_r(t)\right) + \mathbf{K}_r^2\left(\mathbf{x}_r^s(t) - \mathbf{x}_r(t)\right), \tag{6.22a}$$

$$v_m(t) = \dot{m}^s(t) + K_m\left(m^s(t) - m(t)\right), \tag{6.22b}$$

$$\mathbf{v}_{in,c}(t) = \dot{\mathbf{x}}_{in,c}^s(t) + \mathbf{K}_{in,c}\left(\mathbf{x}_{in,c}^s(t) - \mathbf{x}_{in,c}(t)\right). \tag{6.22c}$$

Furthermore, it is possible to prove that this control strategy sets the closed-loop time constants of all the variables. Let us notice that the following equality always holds:

$$\mathbf{h}_x\left(\mathbf{z}_x(t), \mathbf{b}_x(t)\right) := \begin{bmatrix} \mathbf{s}_r(t) - \upsilon\left(\mathbf{n}(t)\right)\boldsymbol{\varphi}\left(\mathbf{n}(t)\right) + \omega(t)\mathbf{x}_r(t) \\ m(t) - \mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{n}(t) \end{bmatrix} = \mathbf{0}_{R+1}, \tag{6.23}$$

where $\mathbf{n}(t)$ is given by Eq. (6.1) and

$$\mathbf{b}_x(t) := \mathbf{x}_{in,n}(t). \tag{6.24}$$

Hence, one can specify the $R+1$ equations $\mathbf{h}_x\left(\mathbf{z}_x(t), \mathbf{b}_x(t)\right) = \mathbf{0}_{R+1}$ in the $2R+n_u+1$ variables $\mathbf{z}_x(t)$ and $\mathbf{b}_x(t)$, where $R+n_u$ of these variables (that is, $\mathbf{z}_x(t)$) are controlled. According to the implicit function theorem, if $\frac{\partial \mathbf{h}_x}{\partial \mathbf{b}_x}\left(\mathbf{z}_x(t), \mathbf{b}_x(t)\right)$ is invertible, $\mathbf{b}_x(t)$ is a unique function of $\mathbf{z}_x(t)$, which implies that the closed-loop time constants of the remaining $R+1$ variables $\mathbf{b}_x(t)$ can also be set. This is equivalent to the existence of an inverse transformation $\mathbf{t}_x^{-1}(\mathbf{z}_x(t))$, which implies that the transformation $\mathbf{t}_x$ is a diffeomorphism. Note that

$$\frac{\partial \mathbf{h}_x}{\partial \mathbf{b}_x}\left(\mathbf{z}_x(t), \mathbf{b}_x(t)\right) = \begin{bmatrix} -\frac{\partial \mathbf{r}_v(t)}{\partial \mathbf{n}}\mathbf{W}_{in}\mathbf{S}_{x,n}^{\mathrm{T}} \\ -\mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{W}_{in}\mathbf{S}_{x,n}^{\mathrm{T}} \end{bmatrix}. \tag{6.25}$$

However, this approach obtains offset-free control of the mass and $n_u - 1$ vessel extents, which is typically not the goal of a control scheme. Ideally, one would like to set the closed-loop time constants of all the variables, while obtaining offset-free control of the mass and $n_u - 1$ numbers of moles. The following section details how it is possible to achieve this.

6.2.3 Offset-free control of numbers of moles

Let us assume that we would like to obtain offset-free control of the mass and $n_u - 1$ numbers of moles, where R of these numbers of moles are $\mathbf{n}_t$, and the remaining $n_u - 1 - R$ numbers of moles are part of $\mathbf{n}_o$ and are denoted $\mathbf{n}_{o,c}$, which implies that $n_u - 1 \geq R$.[4] Let

[4]The numbers of moles with relative degree one with respect to $\mathbf{u}_{in}$ are partitioned as $\mathbf{n}_o(t) = \begin{bmatrix} \mathbf{n}_{o,n}(t) \\ \mathbf{n}_{o,c}(t) \end{bmatrix}$, with $\mathbf{n}_{o,n} = \mathbf{S}_{n,n}\mathbf{n}_o$ of dimension $p - (n_u - 1) + R$ and $\mathbf{n}_{o,c} = \mathbf{S}_{n,c}\mathbf{n}_o$ of dimension $n_u - 1 - R$. If the mass m is not controlled, offset-free control of n_u numbers of moles (instead of $n_u - 1$) can be obtained, and all the occurences of $n_u - 1$ in this section are changed to n_u, but no guarantee can be given regarding the dimension of the system.

us define $\mathbf{s}_t$ as the right-hand side of Eq. (6.7a), that is,

$$\mathbf{s}_t(t) := \boldsymbol{\phi}^{\nu}_{r,t}(t) - \omega(t)\mathbf{n}_t(t). \tag{6.26}$$

One would like to manipulate the p flowrates $\mathbf{u}_{in}$ (and possibly the inverse of the residence time ω) to implement feedback linearization, such that the R numbers of moles $\mathbf{n}_t$, the R rates $\mathbf{s}_t$, the mass m and the $n_u - 1 - R$ numbers of moles $\mathbf{n}_{o,c}$ obey the dynamics

$$\dot{\mathbf{n}}_t(t) = \mathbf{s}_t(t), \tag{6.27a}$$
$$\dot{\mathbf{s}}_t(t) = \mathbf{v}_t(t), \tag{6.27b}$$
$$\dot{m}(t) = v_m(t), \tag{6.27c}$$
$$\dot{\mathbf{n}}_{o,c}(t) = \mathbf{v}_{o,c}(t), \tag{6.27d}$$

where $\mathbf{v}_t(t)$, $v_m(t)$, and $\mathbf{v}_{o,c}(t)$ are new inputs. That is, one would like to obtain

$$\dot{\mathbf{z}}_n(t) = \mathbf{A}\mathbf{z}_n(t) + \mathbf{B}\mathbf{v}_n(t), \tag{6.28}$$

with the $(R + n_u)$-dimensional vector of new states

$$\mathbf{z}_n(t) := \begin{bmatrix} \mathbf{n}_t(t) \\ \mathbf{s}_t(t) \\ m(t) \\ \mathbf{n}_{o,c}(t) \end{bmatrix}, \tag{6.29}$$

the n_u-dimensional vector of new inputs

$$\mathbf{v}_n(t) := \begin{bmatrix} \mathbf{v}_t(t) \\ v_m(t) \\ \mathbf{v}_{o,c}(t) \end{bmatrix}, \tag{6.30}$$

the $(R + n_u) \times (R + n_u)$ state matrix

$$\mathbf{A} := \begin{bmatrix} \mathbf{0}_{R\times R} & \mathbf{I}_R & \mathbf{0}_R & \mathbf{0}_{R\times(n_u-1-R)} \\ \mathbf{0}_{R\times R} & \mathbf{0}_{R\times R} & \mathbf{0}_R & \mathbf{0}_{R\times(n_u-1-R)} \\ \mathbf{0}_R^{\mathrm{T}} & \mathbf{0}_R^{\mathrm{T}} & 0 & \mathbf{0}_{n_u-1-R}^{\mathrm{T}} \\ \mathbf{0}_{(n_u-1-R)\times R} & \mathbf{0}_{(n_u-1-R)\times R} & \mathbf{0}_{n_u-1-R} & \mathbf{0}_{(n_u-1-R)\times(n_u-1-R)} \end{bmatrix}, \tag{6.31}$$

and the $(R + n_u) \times n_u$ input matrix

$$\mathbf{B} := \begin{bmatrix} \mathbf{0}_{R\times R} & \mathbf{0}_R & \mathbf{0}_{R\times(n_u-1-R)} \\ \mathbf{I}_R & \mathbf{0}_R & \mathbf{0}_{R\times(n_u-1-R)} \\ \mathbf{0}_R^{\mathrm{T}} & 1 & \mathbf{0}_{n_u-1-R}^{\mathrm{T}} \\ \mathbf{0}_{(n_u-1-R)\times R} & \mathbf{0}_{n_u-1-R} & \mathbf{I}_{n_u-1-R} \end{bmatrix}, \tag{6.32}$$

which implies that the linear system specified by $\mathbf{A}$ and $\mathbf{B}$ is controllable.

Note that it is possible to compute $\mathbf{z}_n(t)$ from the knowledge of $\mathbf{n}_a(t)$ and $\omega(t)$ if one notes that $\mathbf{n}_t(t)$ and $\mathbf{n}_{o,c}(t)$ are part of $\mathbf{n}_a(t)$ and one uses Eqs. (6.8) and (6.26) for $\mathbf{s}_t(t)$ and Eq. (6.2) for $m(t)$, with $\mathbf{n}(t)$ given by Eq. (6.9). Furthermore, since

$$\begin{aligned}\dot{\mathbf{s}}_t(t) &= \frac{\partial \boldsymbol{\phi}^{\nu}_{r,t}(t)}{\partial \mathbf{n}}\dot{\mathbf{n}}(t) - \omega(t)\dot{\mathbf{n}}_t(t) - \dot{\omega}(t)\mathbf{n}_t(t) \\ &= \frac{\partial \boldsymbol{\phi}^{\nu}_{r,t}(t)}{\partial \mathbf{n}}\left(\mathbf{N}^{\mathrm{T}}\mathbf{r}_{\nu}(t) + \mathbf{W}_{in}\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}(t)\right) - \omega(t)\left(\boldsymbol{\phi}^{\nu}_{r,t}(t) - \omega(t)\mathbf{n}_t(t)\right) \\ &\quad - \dot{\omega}(t)\mathbf{n}_t(t), \end{aligned} \tag{6.33}$$

$$\begin{aligned}\dot{m}(t) &= \mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\left(\mathbf{N}^{\mathrm{T}}\mathbf{r}_{\nu}(t) + \mathbf{W}_{in}\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}(t)\right) \\ &= \mathbf{1}_p^{\mathrm{T}}\mathbf{u}_{in}(t) - \omega(t)m(t), \end{aligned} \tag{6.34}$$

the change of variables $\mathbf{z}_n(t) = \mathbf{t}_n\big(\mathbf{n}_a(t)\big)$ transforms Eqs. (6.7a)-(6.7b) into the form

$$\dot{\mathbf{z}}_n(t) = \mathbf{A}\mathbf{z}_n(t) + \mathbf{B}\Big(\mathbf{Q}_n\big(\mathbf{n}_a(t)\big)\mathbf{u}_{in}(t) + \mathbf{p}_n\big(\mathbf{n}_a(t)\big)\Big), \tag{6.35}$$

with

$$\mathbf{Q}_n\big(\mathbf{n}_a(t)\big) := \begin{bmatrix} \frac{\partial \boldsymbol{\phi}^{\nu}_{r,t}(t)}{\partial \mathbf{n}}\mathbf{W}_{in} \\ \mathbf{1}_p^{\mathrm{T}} \\ \mathbf{S}_{n,c}\mathbf{W}_{in,o} \end{bmatrix}, \tag{6.36a}$$

$$\begin{aligned}\mathbf{p}_n\big(\mathbf{n}_a(t)\big) := &\begin{bmatrix} \frac{\partial \boldsymbol{\phi}^{\nu}_{r,t}(t)}{\partial \mathbf{n}}\mathbf{N}^{\mathrm{T}} \\ \mathbf{0}_R^{\mathrm{T}} \\ \mathbf{S}_{n,c}\mathbf{N}_o^{\mathrm{T}} \end{bmatrix}\mathbf{r}_{\nu}(t) - \omega(t)\begin{bmatrix} \frac{\partial \boldsymbol{\phi}^{\nu}_{r,t}(t)}{\partial \mathbf{n}}\mathbf{n}(t) + \boldsymbol{\phi}^{\nu}_{r,t}(t) - \omega(t)\mathbf{n}_t(t) \\ m(t) \\ \mathbf{n}_{o,c}(t) \end{bmatrix} \\ &- \dot{\omega}(t)\begin{bmatrix} \mathbf{n}_t(t) \\ 0 \\ \mathbf{0}_{n_u-1-R} \end{bmatrix}, \end{aligned} \tag{6.36b}$$

if $\omega(t)$ and its derivative $\dot{\omega}(t)$ are known in advance ($n_u = p$).

Then, the feedback linearization law that achieves the desired linearized dynamics is

$$\mathbf{u}_{in}(t) = \mathbf{Q}_n\big(\mathbf{n}_a(t)\big)^{-1}\Big(\mathbf{v}_n(t) - \mathbf{p}_n\big(\mathbf{n}_a(t)\big)\Big), \tag{6.37}$$

if $n_u = p$.[5]

Eq. (6.27) corresponds to a controllable linear system, where the states are the R numbers of moles $\mathbf{n}_t$, the R rates $\mathbf{s}_t$, the mass m and the $n_u - 1 - R$ numbers of moles $\mathbf{n}_{o,c}$. Then,

[5] If $\omega(t)$ and its derivative $\dot{\omega}(t)$ are also manipulated as part of the control scheme ($n_u = p + 1$), then $\omega(t)$ becomes an additional state of the system, and Eqs. (6.35)–(6.37) are formulated in terms of the manipulated variables $\begin{bmatrix} \mathbf{u}_{in}(t) \\ \dot{\omega}(t) \end{bmatrix}$ instead of $\mathbf{u}_{in}(t)$. Hence, all the results in this section also hold for the case $n_u = p + 1$.

it is possible to set the closed-loop time constants of these $R + n_u$ variables and to obtain offset-free control of the n_u variables $\mathbf{n}_t(t)$, $m(t)$ and $\mathbf{n}_{o,c}(t)$ to the setpoints $\mathbf{n}_t^s(t)$, $m^s(t)$ and $\mathbf{n}_{o,c}^s(t)$ by choosing the feedback control laws

$$\mathbf{v}_t(t) = \dot{\mathbf{n}}_t^s(t) + 2\mathbf{K}_t \left(\dot{\mathbf{n}}_t^s(t) - \boldsymbol{\phi}_{r,t}^v(t) + \omega(t)\mathbf{n}_t(t)\right) + \mathbf{K}_t^2 \left(\mathbf{n}_t^s(t) - \mathbf{n}_t(t)\right), \tag{6.38a}$$

$$v_m(t) = \dot{m}^s(t) + K_m\left(m^s(t) - m(t)\right), \tag{6.38b}$$

$$\mathbf{v}_{o,c}(t) = \dot{\mathbf{n}}_{o,c}^s(t) + \mathbf{K}_{o,c}\left(\mathbf{n}_{o,c}^s(t) - \mathbf{n}_{o,c}(t)\right). \tag{6.38c}$$

Furthermore, it is possible to prove that this control strategy sets the closed-loop time constants of all the variables. Let us notice that the following equality always holds:

$$\mathbf{h}_n\big(\mathbf{z}_n(t), \mathbf{b}_n(t)\big) := \begin{bmatrix} \mathbf{s}_t(t) - \mathbf{N}_t^{\mathrm{T}} \upsilon\big(\mathbf{n}(t)\big)\boldsymbol{\varphi}\big(\mathbf{n}(t)\big) + \omega(t)\mathbf{n}_t(t) \\ m(t) - \mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{n}(t) \end{bmatrix} = \mathbf{0}_{R+1}, \tag{6.39}$$

where $\mathbf{n}(t)$ is given by Eq. (6.9) and

$$\mathbf{b}_n(t) := \mathbf{n}_{o,n}(t). \tag{6.40}$$

Hence, one can specify the $R+1$ equations $\mathbf{h}_n\big(\mathbf{z}_n(t), \mathbf{b}_n(t)\big) = \mathbf{0}_{R+1}$ in the $2R + n_u + 1$ variables $\mathbf{z}_n(t)$ and $\mathbf{b}_n(t)$, where $R + n_u$ of these variables (that is, $\mathbf{z}_n(t)$) are controlled. According to the implicit function theorem, if $\frac{\partial \mathbf{h}_n}{\partial \mathbf{b}_n}\big(\mathbf{z}_n(t), \mathbf{b}_n(t)\big)$ is invertible, $\mathbf{b}_n(t)$ is a unique function of $\mathbf{z}_n(t)$, which implies that the closed-loop time constants of the remaining $R+1$ variables $\mathbf{b}_n(t)$ can also be set. This is equivalent to the existence of an inverse transformation $\mathbf{t}_n^{-1}(\mathbf{z}_n(t))$, which implies that the transformation $\mathbf{t}_n$ is a diffeomorphism. Note that

$$\frac{\partial \mathbf{h}_n}{\partial \mathbf{b}_n}\big(\mathbf{z}_n(t), \mathbf{b}_n(t)\big) = \begin{bmatrix} -\frac{\partial \boldsymbol{\phi}_{r,t}^v(t)}{\partial \mathbf{n}} \mathscr{L}\mathscr{T}_o \mathbf{S}_{n,n}^{\mathrm{T}} \\ -\mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w \mathscr{L}\mathscr{T}_o \mathbf{S}_{n,n}^{\mathrm{T}} \end{bmatrix}. \tag{6.41}$$

6.2.4 Simulated example

This section shows the performance of the proposed control scheme for a simulated reaction system. This reaction system corresponds to a continuous homogeneous reactor with $S = 5$ species (A, B, C, D, and the solvent S), where the density and residence time are constant and equal to 1 kg/L and 10 min, respectively, and the $R = 2$ reactions A + B $\rightarrow$ C and 2 B $\rightarrow$ D take place. This reactor is fed with $p = 3$ inlet streams, where the first contains solvent and A with a composition of 1.5 mol/kg, the second contains solvent and B with a composition of 2.0 mol/kg, and the third contains only solvent. Furthermore, the reaction rates are $r_{v,1} = k_1 n_{\mathrm{A}} n_{\mathrm{B}}/V$ and $r_{v,2} = k_2 n_{\mathrm{B}}^2/V$, with $k_1 = 0.053$ L/mol/min and $k_2 = 0.128$ L/mol/min.

Since the residence time is constant and known, the inverse of the residence time and its derivative are known in advance, and we have the case $n_u = p = 3$. The system starts at the

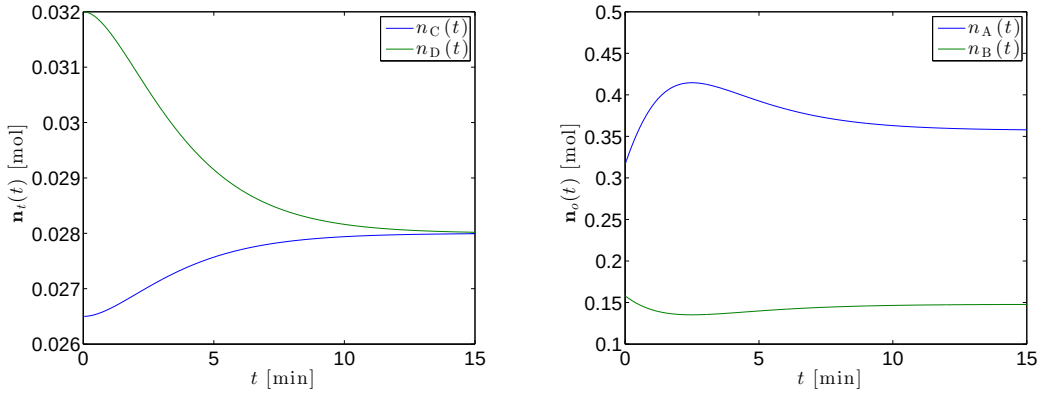

Figure 6.1 – Trajectories of (i) the numbers of moles with relative degree two with respect to the inlet flowrates at left, and (ii) the numbers of moles with relative degree one with respect to the inlet flowrates at right.

steady state that corresponds to the mass $m = 1$ kg and the numbers of moles $n_C = 0.0265$ mol and $n_D = 0.032$ mol. The objective of the control scheme is to obtain offset-free control of the $R = n_u - 1 = 2$ numbers of moles $\mathbf{n}_t = \begin{bmatrix} n_C \\ n_D \end{bmatrix}$ and the mass m and to set the closed-loop time constants of all the variables (including the p numbers of moles $\mathbf{n}_o = \begin{bmatrix} n_A \\ n_B \\ n_S \end{bmatrix}$) as described in Section 6.2.3, such that the system is driven to a new steady state within 15 min. More precisely, at the initial time, the setpoint m^s remains equal to 1 kg and the setpoints $\mathbf{n}_t^s$ become equal to $\begin{bmatrix} 0.028 \\ 0.028 \end{bmatrix}$ mol, while the closed-loop time constants of the variables $m(t)$ and $\mathbf{n}_t(t)$ are set to 2 min by choosing $K_m = 1/2$ min^{-1} and $\mathbf{K}_t = \begin{bmatrix} 1/2 & 0 \\ 0 & 1/2 \end{bmatrix}$ min^{-1}.

The state trajectories for this simulated example are shown in Figure 6.1. One can observe that the variables $\mathbf{n}_t(t)$ follow the trajectory of a critically damped second-order system until they reach the steady state that corresponds to the setpoints $\mathbf{n}_t^s$. At the same time, the variables $\mathbf{n}_o(t)$ also converge to steady state within the specified time. The mass remains constant and equal to 1 kg throughout the 15 min of this simulation (results not shown). The inlet flowrates that are manipulated to fulfill these control objectives are shown in Figure 6.2. It is also possible to see that these inlet flowrates become constant after 15 min.

6.3 Control without Kinetic Models

6.3.1 System description

Let us recall the dynamic model presented in Eq. (5.1) for the available states $\mathbf{y}(t)$. Let us suppose that, out of the available states $\mathbf{y}(t)$, one would like to control an n_x-dimensional vector of available states $\mathbf{x}(t)$. The n_u inputs $\mathbf{u}(t)$ can be seen as additional rates whose

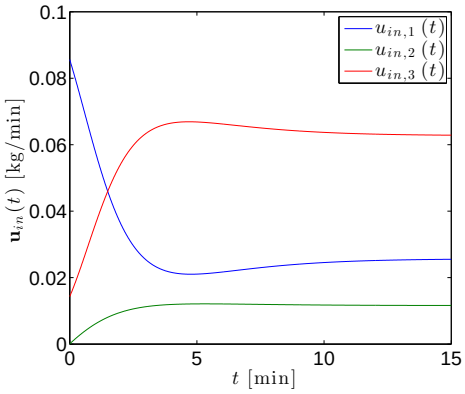

Figure 6.2 – Trajectories of the inlet flowrates.

values are known and can be manipulated, at least indirectly. Furthermore, in addition to the structure of the dynamic model for $\mathbf{y}(t)$ presented in Eq. (5.1), it is assumed that (i) the known part of the dynamic model for $\mathbf{x}(t)$ is affine in $\mathbf{u}(t)$, and (ii) the unknown part is independent of $\mathbf{u}(t)$ and depends only on $\mathbf{x}(t)$. This implies that one can write

$$\dot{\mathbf{x}}(t) = \mathbf{F}\mathbf{r}_u\big(\mathbf{x}(t)\big) + \boldsymbol{\beta}_a\big(\mathbf{y}(t)\big) + \mathbf{B}_a\big(\mathbf{y}(t)\big)\mathbf{u}(t), \qquad \mathbf{x}(0) = \mathbf{x}_0. \tag{6.42}$$

If

$$\operatorname{rank}\big(\mathbf{B}_a\big(\mathbf{y}(t)\big)\big) = n_x = n_u, \tag{6.43}$$

it is possible to find an $n_x \times n_x$ matrix $\mathbf{U}_a$ such that

$$\mathbf{U}_a(t) = \mathbf{B}_a\big(\mathbf{y}(t)\big)^{-1}. \tag{6.44}$$

The objective is to control the variables $\mathbf{x}(t)$ to the setpoints $\mathbf{x}^s(t)$ by manipulating the variables $\mathbf{u}(t)$. The proposed control scheme includes two steps, namely, the estimation of the unknown rates shown before and the control of $\mathbf{x}(t)$ via feedback linearization.

6.3.2 Control via feedback linearization and rate estimation

The task of the controller consists in forcing the convergence of the controlled variables $\mathbf{x}(t)$ towards their reference trajectories $\mathbf{x}^s(t)$.

The controller described in this subsection can be seen as the implementation of an approach that builds on input-output feedback linearization. For this, the new inputs $\mathbf{v}(t)$ are defined as an approximation of the right-hand side of the dynamic equations of $\mathbf{x}(t)$ in Eq. (6.42). This approximation consists in replacing $\boldsymbol{\beta}_a\big(\mathbf{y}(t)\big)$ by $\tilde{\boldsymbol{\beta}}_a(t)$, $\mathbf{r}_u\big(\mathbf{x}(t)\big)$ by $\hat{\mathbf{r}}_u(t)$,

and $\mathbf{B}_a\big(\mathbf{y}(t)\big)$ by $\tilde{\mathbf{B}}_a(t)$, which yields

$$\mathbf{v}(t) = \tilde{\mathbf{w}}(t) + \tilde{\mathbf{B}}_a(t)\mathbf{u}(t), \tag{6.45}$$

with

$$\tilde{\mathbf{w}}(t) = \mathbf{F}\hat{\mathbf{r}}_u(t) + \tilde{\boldsymbol{\beta}}_a(t), \tag{6.46}$$

which is the approximation of

$$\mathbf{w}(t) = \mathbf{F}\mathbf{r}_u\big(\mathbf{x}(t)\big) + \boldsymbol{\beta}_a\big(\mathbf{y}(t)\big). \tag{6.47}$$

For the sake of simplicity, the functions $\mathbf{r}_u\big(\mathbf{x}(t)\big)$, $\boldsymbol{\beta}_a\big(\mathbf{y}(t)\big)$, and $\mathbf{B}_a\big(\mathbf{y}(t)\big)$ are denoted as time-variant signals $\mathbf{r}_u(t)$, $\boldsymbol{\beta}_a(t)$, and $\mathbf{B}_a(t)$ in the remainder of this section.

It is assumed here that the actuators possess first-order dynamics. Let $\mathbf{T}_a$ be the n_u-dimensional diagonal matrix of time constants of the actuators and h the sampling period, which means that there exists an actuator input $\bar{\mathbf{u}}(t)$ such that, for all $\zeta \in [0,h)$,

$$\mathbf{u}(t+\zeta) = \bar{\mathbf{u}}(t) + \exp\left(-\mathbf{T}_a^{-1}\zeta\right)\left(\mathbf{u}(t) - \bar{\mathbf{u}}(t)\right). \tag{6.48}$$

Moreover, the controller outputs are denoted as $\tilde{\bar{\mathbf{u}}}(t)$, with the difference between the controller outputs and the actuator inputs given by the disturbance variables

$$\mathbf{d}_{\bar{\mathbf{u}}}(t) = \tilde{\bar{\mathbf{u}}}(t) - \bar{\mathbf{u}}(t). \tag{6.49}$$

Then, the relationship between the new inputs $\mathbf{v}(t)$ and the manipulated variables $\tilde{\bar{\mathbf{u}}}(t)$ is known. To acknowledge that fact, one solves Eq. (6.45) for $\mathbf{u}(t)$ and assigns the result to a weighted average of $\mathbf{u}(t+\zeta)$ and $\bar{\mathbf{u}}(t+\zeta)$ for ζ in $[0,h)$, which results in

$$h^{-1}\int_0^h \left(\left(\mathbf{I}_{n_x} - \mathbf{D}\right)\bar{\mathbf{u}}(t+\zeta) + \mathbf{D}\mathbf{u}(t+\zeta)\right)\mathrm{d}\zeta = \tilde{\mathbf{B}}_a(t)^{-1}\left(\mathbf{v}(t) - \tilde{\mathbf{w}}(t)\right), \tag{6.50}$$

where $\mathbf{D}$ is a constant, diagonal n_x-dimensional matrix of desired reduction of the time constants of the actuators.

Then, if Eq. (6.48) is replaced in the equation above and the resulting integral is solved, that leads to

$$\bar{\mathbf{u}}(t) + \mathbf{D}\mathbf{T}_a h^{-1}\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{u}(t) - \bar{\mathbf{u}}(t)\right) = \tilde{\mathbf{B}}_a(t)^{-1}\left(\mathbf{v}(t) - \tilde{\mathbf{w}}(t)\right). \tag{6.51}$$

Finally, if one solves for $\bar{\mathbf{u}}(t)$, the result is

$$\bar{\mathbf{u}}(t) = \left(\mathbf{I}_{n_x} + \mathbf{W}\right)\tilde{\mathbf{B}}_a(t)^{-1}\left(\mathbf{v}(t) - \tilde{\mathbf{w}}(t)\right) - \mathbf{W}\mathbf{u}(t), \tag{6.52}$$

where

$$\mathbf{W} = \left(\mathbf{I}_{n_x} - \mathbf{D}\mathbf{T}_a h^{-1}\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\right)^{-1}\mathbf{D}\mathbf{T}_a h^{-1}\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right), \quad (6.53)$$

which is equivalent to the feedback linearization law in the next proposition if $\bar{\mathbf{u}}(t)$ and $\mathbf{u}(t)$ are replaced by $\tilde{\bar{\mathbf{u}}}(t)$ and $\tilde{\mathbf{u}}(t)$, respectively.

Hence, the control law for the controller outputs $\tilde{\bar{\mathbf{u}}}(t)$ and its influence on the inputs $\mathbf{u}(t+h)$ and the controlled variables $\mathbf{x}(t+h)$ are given as follows.

Proposition 6.1. *Let the rank condition in Eq.* (6.43) *and the assumptions of Proposition 5.3 be satisfied,* $\mathbf{r}_u$ *be Lipschitz continuous, and the controller outputs be given by*

$$\tilde{\bar{\mathbf{u}}}(t) = \left(\mathbf{I}_{n_x} + \mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\left(\mathbf{v}(t) - \tilde{\boldsymbol{\beta}}_a(t) - \mathbf{F}\hat{\mathbf{r}}_u(t)\right) - \mathbf{W}\tilde{\mathbf{u}}(t), \quad (6.54)$$

where

$$\tilde{\mathbf{U}}_a(t) = \tilde{\mathbf{B}}_a(t)^{-1} = \mathbf{U}_a(t)\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right). \quad (6.55)$$

Then, $\mathbf{u}(t+h)$ *and* $\mathbf{x}(t+h)$ *are given by Eqs.* (E.1) *and* (E.2)*, where*

$$\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t) = \mathbf{d}_{\boldsymbol{\beta}_a}(t) + \tilde{\mathbf{U}}_a(t)^{-1}\left(\mathbf{I}_{n_x} + \mathbf{W}\right)^{-1}\left(\mathbf{d}_{\tilde{\mathbf{u}}}(t) + \mathbf{W}\mathbf{d}_{\mathbf{u}}(t)\right), \quad (6.56)$$

assuming that, for all ζ *in* $[0,h)$*,* $\mathbf{B}_a(t+\zeta)$ *and* $\boldsymbol{\beta}_a(t+\zeta)$ *remain constant.*

Proof. See Appendix E.1. □

Simultaneously, $\mathbf{v}(t)$ should be defined according to an outer-loop feedback control strategy that forces the controlled variables $\mathbf{x}(t)$ to converge towards their reference trajectories $\mathbf{x}^s(t)$ at a desired rate and ensures that the controlled variables are stable. Such a strategy is described below, in two steps: the first step shows the result of the application of the controller in the discrete-time case, while the second step shows the same result in the continuous-time case, when the sampling period h tends to zero.

Proposition 6.2. *Let* $\boldsymbol{\Gamma}$ *be a constant, diagonal positive definite* n_x*-dimensional matrix of desired exponential convergence rates for the variables* $\mathbf{x}(t)$ *and the conditions in Proposition 6.1 and in Eqs.* (5.3) *and* (5.4) *be satisfied, and let us assume that*

$$\mathbf{v}(t) = \frac{\mathbf{x}^s(t+h) - \mathbf{x}^s(t)}{h} + \boldsymbol{\Gamma}\left(\mathbf{x}^s(t) - \tilde{\mathbf{x}}(t)\right). \quad (6.57)$$

Then, if

$$\mathbf{D} = \mathbf{I}_{n_x}, \quad (6.58)$$

the expected value of $\mathbf{x}(t)$ *is given by*

$$\begin{aligned}
&\mathrm{E}\left[\mathbf{x}(t)\right] \\
&= \mathbf{x}^s(t) + \left(\mathbf{I}_{n_x} - h\boldsymbol{\Gamma}\right)^n \left(\mathbf{x}(t-nh) - \mathbf{x}^s(t-nh)\right) \\
&\quad + \sum_{m=1}^{n} \left(\mathbf{I}_{n_x} - h\boldsymbol{\Gamma}\right)^{m-1} h^2 \mathbf{F} \left(\sum_{k=0}^{q-2} b_{k+1} \int_k^{k+1} \dot{\mathbf{r}}_u(t - mh - \Delta t + \xi h)(\xi - k)\,\mathrm{d}\xi \right) \\
&\quad + \sum_{m=1}^{n} \left(\mathbf{I}_{n_x} - h\boldsymbol{\Gamma}\right)^{m-1} h^2 \mathbf{F} \left(\sum_{k=0}^{q-2} b_{k+1} \int_{k+1}^{q-1} \dot{\mathbf{r}}_u(t - mh - \Delta t + \xi h)\mathrm{d}\xi \right) \\
&\quad + \sum_{m=1}^{n} \left(\mathbf{I}_{n_x} - h\boldsymbol{\Gamma}\right)^{m-1} h^2 \mathbf{F} \int_0^1 (1-\xi)\,\dot{\mathbf{r}}_u(t - mh + \xi h)\mathrm{d}\xi,
\end{aligned} \tag{6.59}$$

with

$$\dot{\mathbf{r}}_u(t) = \frac{\mathrm{d}\mathbf{r}_u(t)}{\mathrm{d}t} = \frac{\partial \mathbf{r}_u}{\partial \mathbf{x}}(t)\dot{\mathbf{x}}(t), \tag{6.60}$$

whereas the i*th diagonal element of the covariance matrix of* $\mathbf{x}(t)$ *is given by*

$$\begin{aligned}
\sigma_{x_i}^2 &= \frac{h^2 \boldsymbol{\Gamma}_{i,i}^2 \left(1 - \left(1 - h\boldsymbol{\Gamma}_{i,i}\right)^{2n}\right)}{1 - \left(1 - h\boldsymbol{\Gamma}_{i,i}\right)^2} \mathrm{Var}\left[d_{x_i}(t) + \boldsymbol{\Gamma}_{i,i}^{-1} d_{\tilde{\beta}_{a,i}}(t) \right] \\
&\quad + \frac{\beta_q(1 - h\boldsymbol{\Gamma}_{i,i}, 1 - h\boldsymbol{\Gamma}_{i,i}, n)}{1 - \left(1 - h\boldsymbol{\Gamma}_{i,i}\right)^2} \left(\mathbf{F}\boldsymbol{\mathscr{T}}\right)_i \mathrm{Var}\left[\mathbf{d}_{\mathbf{y}}(t)\right] \left(\mathbf{F}\boldsymbol{\mathscr{T}}\right)_i^{\mathrm{T}} \\
&\quad + 2\frac{h\boldsymbol{\Gamma}_{i,i}\gamma_q(1 - h\boldsymbol{\Gamma}_{i,i}, 1 - h\boldsymbol{\Gamma}_{i,i}, n)}{1 - \left(1 - h\boldsymbol{\Gamma}_{i,i}\right)^2} \mathrm{Cov}\left[d_{x_i}(t) + \boldsymbol{\Gamma}_{i,i}^{-1} d_{\tilde{\beta}_{a,i}}(t), \mathbf{d}_{\mathbf{y}}(t) \right] \left(\mathbf{F}\boldsymbol{\mathscr{T}}\right)_i^{\mathrm{T}}, \\
&\quad i = 1, \ldots, n_x,
\end{aligned} \tag{6.61}$$

assuming that the noise in $\tilde{\mathbf{U}}_a(t)$ *is negligible.*

Proof. See Appendix E.2. □

Proposition 6.3. *Let the conditions of Proposition 6.2 be satisfied and* $h \to 0$*. If* $\mathbf{D} = \mathbf{I}_{n_x}$*, then*

$$\lim_{h \to 0} \mathrm{E}\left[\dot{\mathbf{x}}(t)\right] = \mathrm{E}\left[\mathbf{v}(t)\right], \tag{6.62}$$

and each variable $x_i(t)$ *is expected to decay exponentially to its setpoint* $x_i^s(t)$*, for* $i = 1, \ldots, n_x$*, with time constant equal to* $\frac{1}{\boldsymbol{\Gamma}_{i,i}}$*.*

Finally, if $\mathbf{D} = \mathbf{I}_{n_x}$*, the following result is verified:*

$$\lim_{h \to 0} \sigma_{x_i}^2 = 0, \quad i = 1, \ldots, n_x. \tag{6.63}$$

Proof. See Appendix E.3. □

In Figure 6.3, one can see that the proposed control scheme includes three steps, namely, the estimation of the unknown rates, feedback linearization and feedback control.

Remark 6.1. The fact that this control scheme is based on input-output feedback linearization becomes clear if one observes that the manipulated rates $\tilde{\tilde{\mathbf{u}}}(t)$ given by Eq. (6.54) can be written as an affine function of the new inputs $\mathbf{v}(t)$,

$$\tilde{\tilde{\mathbf{u}}}(t) = \left(\mathbf{I}_{n_x} + \mathbf{W}\right) \tilde{\mathbf{U}}_a(t) \left(\mathbf{v}(t) - \tilde{\mathbf{w}}(t)\right) - \mathbf{W}\tilde{\mathbf{u}}(t), \tag{6.64}$$

which results, when the condition in Eq. (6.58) is satisfied, in an integral relationship between the new inputs $\mathbf{v}(t)$ and the controlled variables $\mathbf{x}(t)$, given by Eq. (6.62) in the continuous-time case. This implies that one can design a feedback controller that forces each element of the vector of control errors $\mathbf{x}^s(t) - \mathbf{x}(t)$ to converge exponentially to zero with time constants given by the corresponding elements of the diagonal of $\mathbf{\Gamma}^{-1}$, by using the control laws in Eqs. (6.54) and (6.57). Note that the latter control law uses $\mathbf{x}^s(t+h)$, which ideally requires prior knowledge of the reference signals $\mathbf{x}^s(t)$.

Remark 6.2. For some variables in $\mathbf{y}(t)$, it may not be possible to include them in $\mathbf{x}(t)$ such that Eqs. (6.42) and (6.43) hold simultaneously. In that case, an alternative is the use of a cascade control scheme, which consists in (i) controlling $\mathbf{x}(t)$ via rate estimation and feedback linearization in the inner loop, and (ii) controlling some of the remaining states $\mathbf{y}(t)$ via proportional-integral (PI) control in the outer loop, denoted as the $n_{y,o}$-dimensional vector $\mathbf{y}_o(t)$ with setpoints $\mathbf{y}_o^s(t)$. In the particular case of reactor control, one can control the temperature and reactant concentrations via rate estimation and feedback linearization in the inner loop, as shown in the example of Section 6.3.4, while the product concentrations are controlled in the outer loop, which is not illustrated by any example in this chapter. A way to construct such a cascade control scheme is to use an outer-loop feedback control law such as

$$\dot{\mathbf{x}}^s(t) = \begin{bmatrix} \dot{\mathbf{x}}_o^s(t) \\ \mathbf{K}_o \left(\mathbf{y}_o^s(t) - \tilde{\mathbf{y}}_o(t) + \mathbf{T}_{i,o}^{-1} \int_0^t \left(\mathbf{y}_o^s(\tau) - \tilde{\mathbf{y}}_o(\tau) \right) \mathrm{d}\tau \right) \end{bmatrix}, \quad \mathbf{x}^s(0) = \mathbf{x}_0^s, \tag{6.65}$$

with the $n_{y,o}$-dimensional diagonal matrices $\mathbf{K}_o$ and $\mathbf{T}_{i,o}$ of controller gains and integral times and the $(n_x - n_{y,o})$-dimensional vector $\mathbf{x}_o(t)$ of selected components of $\mathbf{x}(t)$ with setpoints $\mathbf{x}_o^s(t)$, which implies that offset-free control of the $n_x = n_u$ variables $\mathbf{x}_o(t)$ and $\mathbf{y}_o(t)$ is guaranteed. In Figure 6.4, one can see the proposed cascade control scheme, which includes an outer-loop feedback controller, in addtion to the estimation of the unknown rates, feedback linearization, and inner-loop feedback control already shown in Figure 6.3.

6.3.3 Stability

The results given in Eqs. (6.59) and (6.61) provide a way to assess the stability of the controlled variables $\mathbf{x}(t)$. Let $\mathscr{M}$ be the set of all the models that can describe the unknown

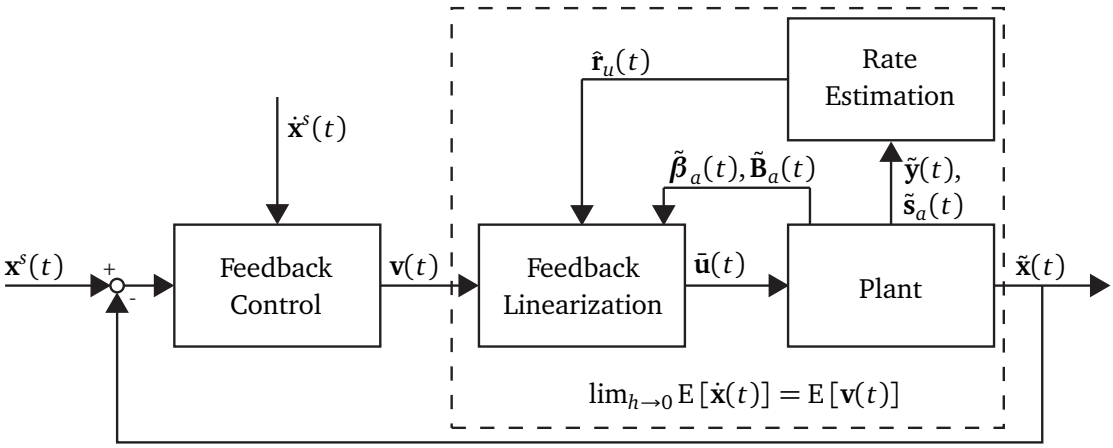

Figure 6.3 – Control based on feedback linearization and estimation of the unknown rates.

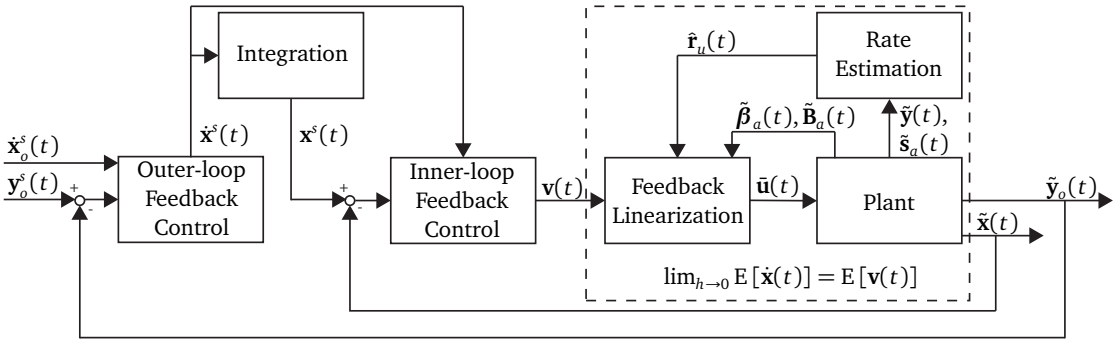

Figure 6.4 – Cascade control based on feedback linearization and estimation of the unknown rates.

rates $\mathbf{r}_u\big(\mathbf{x}(t)\big)$. For each model $m \in \mathscr{M}$, let $\Theta(m) \subset \mathbb{R}^{n_p(m)}$ denote the set that contains all the possible values of the $n_p(m)$ parameters of that model. Finally, let $\Psi \subset \mathbb{R} \times \mathbb{R}^{n_y}$ denote the set of all the admissible trajectories of the available states $\big(t, \mathbf{y}(t)\big)$ and $\Phi \subset \mathbb{R} \times \mathbb{R}^{n_y}$ denote the admissible trajectories of the available rates $\big(t, \mathbf{s}_a(t)\big)$. One can assess stability of $\mathbf{x}(t)$ by verifying the condition

$$\big(\forall_{\tau<t} \parallel \mathbf{x}(\tau) - \mathbf{x}^s(\tau) \parallel_\infty < L\big) \Rightarrow \parallel \mathrm{E}\left[\mathbf{x}(t)\right] + \alpha\boldsymbol{\sigma}_{\mathbf{x}} - \mathbf{x}^s(t) \parallel_\infty < L, \tag{6.66}$$

for some L and all $m \in \mathscr{M}, \boldsymbol{\theta} \in \Theta(m), \big(t, \mathbf{y}(t)\big) \in \Psi, \big(t, \mathbf{s}_a(t)\big) \in \Phi$ and $\alpha \in \mathscr{A}$, where the set $\mathscr{A}$ specifies the probability of maintaining $\parallel \mathbf{x}(t) - \mathbf{x}^s(t) \parallel_\infty < L$.

6.3.4 Simulated example

Let us consider the simulation of a system that consists of a jacketed homogeneous CSTR (that is, an open homogeneous reactor of constant volume) with S species, R independent reactions, p inlet streams and one outlet stream. According to Section 2.2, the states are the S-dimensional vector of numbers of moles $\mathbf{n}(t)$ and the heat of the reaction mixture

$$Q(t) = m(t)c_p(t)\left(T(t) - T_{ref}\right), \tag{6.67}$$

where $T(t)$ is the temperature of the reaction mixture, T_{ref} is the temperature of the reference state, which corresponds to the liquid state at 1 bar and 298.15 K,

$$m(t) = \mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{n}(t) \tag{6.68}$$

is the total mass in the reactor, with $\mathbf{M}_w$ being the S-dimensional diagonal matrix of molecular weights of the species in the reactor, and

$$c_p(t) = \frac{\mathbf{c}_p^{\mathrm{T}}\mathbf{n}(t)}{m(t)} \tag{6.69}$$

is the specific heat capacity at constant pressure of the reaction mixture, with $\mathbf{c}_p$ being the S-dimensional vector of molar heat capacities of the species in the reactor.

One can also consider as an additional state the heat of the jacket

$$Q_j(t) = m_j c_{p,j}\left(T_j(t) - T_{ref}\right), \tag{6.70}$$

where m_j is the total mass of the jacket, $c_{p,j}$ is the specific heat capacity at constant pressure of the jacket, and $T_j(t)$ is the mean temperature of the jacket.

Then, the mole and heat balances of the reactor can be written as

$$\underbrace{\begin{bmatrix}\dot{Q}(t)\\ \dot{\mathbf{n}}(t)\end{bmatrix}}_{\dot{\mathbf{y}}(t)} = \underbrace{\begin{bmatrix}-\Delta\mathbf{H}_r^{\mathrm{T}}\\ \mathbf{N}^{\mathrm{T}}\end{bmatrix}}_{\mathscr{A}}\mathbf{r}_v(t) + \underbrace{\begin{bmatrix}1\\ \mathbf{0}_S\end{bmatrix}}_{\mathbf{b}}q_{ex}(t) + \underbrace{\begin{bmatrix}\check{\mathbf{T}}_{in}^{\mathrm{T}}\\ \mathbf{W}_{in}\end{bmatrix}}_{\mathscr{C}}\mathbf{u}_{in}(t) - \omega(t)\underbrace{\begin{bmatrix}Q(t)\\ \mathbf{n}(t)\end{bmatrix}}_{\mathbf{y}(t)},$$
$$\underbrace{\begin{bmatrix}Q(0)\\ \mathbf{n}(0)\end{bmatrix}}_{\mathbf{y}(0)} = \underbrace{\begin{bmatrix}Q_0\\ \mathbf{n}_0\end{bmatrix}}_{\mathbf{y}_0}, \tag{6.71}$$

with

$$q_{ex}(t) := UA\left(T_j(t) - T(t)\right) + q_{ex,rem}(t), \tag{6.72}$$

and the heat balance of the jacket can be written as

$$\dot{Q}_j(t) = u_j(t)c_{p,j}\Delta T_j(t) - UA\left(T_j(t) - T(t)\right), \tag{6.73}$$

where $\mathbf{N}$ is the $R \times S$ stoichiometric matrix, $\mathbf{W}_{in}$ is the $S \times p$ inlet-composition matrix, $\Delta\mathbf{H}_r$ is the R-dimensional vector of enthalpies of reaction, $\check{\mathbf{T}}_{in}$ is the p-dimensional vector of inlet specific heats, $\mathbf{r}_v(t)$ is the R-dimensional vector of overall reaction rates, U and A are the overall heat transfer coefficient and the heat transfer area of the jacket, respectively, $q_{ex,rem}(t)$ is the heat power that is exchanged with the remaining environment, $\mathbf{u}_{in}(t)$ is the p-dimensional vector of inlet flowrates, $\omega(t) := \frac{u_{out}(t)}{m(t)}$ is the inverse of the residence time, with $u_{out}(t)$ the outlet flowrate, $u_j(t)$ is the inlet flowrate of the jacket, and $\Delta T_j(t)$ is the difference between the temperatures of the inlet and the outlet of the jacket. The state vector $\mathbf{y}(t)$ and the vector $\mathbf{b}$ are both of dimension $S+1$, while the matrix $\mathscr{A}$ has dimension $(S+1) \times R$ and the matrix $\mathscr{C}$ has dimension $(S+1) \times p$.

In this system that consists of a jacketed reactor, the manipulated variables correspond to the inlet flowrate of the jacket $u_j(t)$ and the inlet flowrates $\mathbf{u}_{in}(t)$. We would like to control the heat $Q(t)$ and certain elements of the vector of numbers of moles $\mathbf{n}(t)$. However, since $u_j(t)$ does not affect directly $Q(t)$ and $\mathbf{n}(t)$, at first sight it is not possible to satisfy the condition in Eq. (6.43), which is required for this control scheme without kinetic models.

To solve this problem, one can consider the jacket as an actuator with first-order dynamics. For this, let us define $q_{ex,j}(t) := UA\left(T_j(t) - T_{ref}\right)$ and $q_{ex,r}(t) := UA\left(T(t) - T_{ref}\right)$, which implies that

$$q_{ex}(t) = q_{ex,j}(t) - q_{ex,r}(t) + q_{ex,rem}(t). \tag{6.74}$$

Then, one can observe that the actuator output $q_{ex,j}(t)$ not only affects directly $Q(t)$ but

also possesses first-order dynamics since

$$\begin{aligned}\dot{q}_{ex,j}(t) &= UA\dot{T}_j(t)\\ &= \frac{UA\dot{Q}_j(t)}{m_j c_{p,j}}\\ &= \frac{UA}{m_j c_{p,j}}\left(u_j(t)c_{p,j}\Delta T_j(t) - q_{ex,j}(t) + q_{ex,r}(t)\right)\\ &= T_{a,Q}^{-1}\left(\bar{q}_{ex,j}(t) - q_{ex,j}(t)\right),\end{aligned} \tag{6.75}$$

with the time constant

$$T_{a,Q} := \frac{m_j c_{p,j}}{UA}, \tag{6.76}$$

and the actuator input

$$\bar{q}_{ex,j}(t) := u_j(t)c_{p,j}\Delta T_j(t) + q_{ex,r}(t), \tag{6.77}$$

which can be related to the manipulated variable $u_j(t)$ if $\Delta T_j(t)$ and $q_{ex,r}(t)$ are measured.

The corresponding measured quantities are given by

$$\tilde{q}_{ex,j}(t) = UA\left(\tilde{T}_j(t) - T_{ref}\right), \tag{6.78}$$

$$\tilde{q}_{ex,r}(t) = UA\left(\tilde{T}(t) - T_{ref}\right), \tag{6.79}$$

$$\tilde{\bar{q}}_{ex,j}(t) = \tilde{u}_j(t)c_{p,j}\Delta\tilde{T}_j(t) + \tilde{q}_{ex,r}(t), \tag{6.80}$$

which implies that the controller output $\tilde{\bar{q}}_{ex,j}(t)$ can be enforced by manipulating

$$\tilde{u}_j(t) = \frac{\tilde{\bar{q}}_{ex,j}(t) - \tilde{q}_{ex,r}(t)}{c_{p,j}\Delta\tilde{T}_j(t)}. \tag{6.81}$$

It is assumed that the constant reactor volume $V(t)$ is given by the sum of the mass of the individual species divided by the constant density of the reaction mixture ρ, that is,

$$V(t) = \frac{\mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w}{\rho}\mathbf{n}(t) = \frac{\mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w}{\rho}\mathbf{n}_0. \tag{6.82}$$

In a homogeneous CSTR, since

$$\mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{N}^{\mathrm{T}} = \mathbf{0}_R^{\mathrm{T}}, \tag{6.83}$$

$$\mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{W}_{in} = \mathbf{1}_p^{\mathrm{T}}, \tag{6.84}$$

$$\mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{n}_0 = m_0, \tag{6.85}$$

Table 6.1 – Values of the molecular weights of species A, B, C, and D.

Species	A	B	C	D
m_w [kg kmol^{-1}]	67.09	84.08	151.17	168.16

Table 6.2 – Values of the rate constants of reactions R1 and R2.

Reaction	R1	R2
A [l kmol^{-1} s^{-1}]	1.692×10^5	7.232×10^3
E_a [kJ kmol^{-1}]	20000	10000

the inverse of the residence time is

$$\omega(t) = \frac{\mathbf{1}_p^{\mathrm{T}}}{m_0}\mathbf{u}_{in}(t) = \mathbf{k}_{in}^{\mathrm{T}}\mathbf{u}_{in}(t), \tag{6.86}$$

thereby keeping the volume constant as follows:

$$\begin{aligned}\dot{V}(t) = \frac{\mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w}{\rho}\dot{\mathbf{n}}(t) = \frac{\mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w}{\rho}\left(\mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}\mathbf{u}_{in}(t)\right) - V(t)\omega(t) = \frac{\mathbf{1}_p^{\mathrm{T}}\mathbf{u}_{in}(t) - m_0\omega(t)}{\rho} \\ = 0.\end{aligned} \tag{6.87}$$

In this particular simulated example, let us consider the acetoacetylation of pyrrole in a homogeneous reactor of constant volume with $S = 4$ species (A: pyrrole; B: diketene; C: 2-acetoacetylpyrrole; D: dehydroacetic acid), $R = 2$ reactions (A + B $\rightarrow$ C, 2B $\rightarrow$ D), $p = 2$ inlets (of A and B) and 1 outlet, the flowrate of which is adjusted to keep the volume constant [114].

For this simulation, the following values are used: $\mathbf{N} = \left[\begin{smallmatrix} -1 & -1 & 1 & 0 \\ 0 & -2 & 0 & 1 \end{smallmatrix}\right]$, $\Delta\mathbf{H}_r = \left[\begin{smallmatrix} -70 \\ -50 \end{smallmatrix}\right] \times 10^3$ kJ kmol^{-1}, $\mathbf{W}_{in}^{\mathrm{T}} = \left[\begin{smallmatrix} 67.09^{-1} & 0 & 0 & 0 \\ 0 & 84.08^{-1} & 0 & 0 \end{smallmatrix}\right]$ kmol kg^{-1}, $\check{\mathbf{T}}_{in} = \mathbf{0}_p$ at $T_{ref} = 298.15$ K, $r_{v,1} = Vk_1c_{\mathrm{A}}c_{\mathrm{B}}$, $r_{v,2} = Vk_2c_{\mathrm{B}}^2$, where $\mathbf{c}(t) = \mathbf{n}(t)/V(t)$, $k_1 = A_1 \exp\left(-\frac{E_{a,1}}{RT}\right)$, $k_2 = A_2 \exp\left(-\frac{E_{a,2}}{RT}\right)$. The values of the molecular weights of these species are given in Table 6.1, and all the necessary information about the reactions R1 and R2, namely the values of A_1, A_2, $E_{a,1}$, $E_{a,2}$, is provided in Table 6.2. The volume is constant at $V = 90.16$ L. Furthermore, it is assumed that the density and the specific heat capacity are constant and equal to 0.9978 kg L^{-1} and 1.439 kJ kg^{-1} K^{-1}, respectively, which results in the constant heat capacity $mc_p = 129.5$ kJ K^{-1}.

The system is initially at steady state corresponding to the inputs $\bar{q}_{ex} = -4.9 \times 10^3$ kJ min^{-1} and $\bar{\mathbf{u}}_{in} = \left[\begin{smallmatrix} \bar{u}_{in,\mathrm{A}} \\ \bar{u}_{in,\mathrm{B}} \end{smallmatrix}\right] = \left[\begin{smallmatrix} 40 \\ 15 \end{smallmatrix}\right]$ kg min^{-1}, which corresponds to the initial values $\mathbf{n}_0^{\mathrm{T}} =$

$[0.833\ \ 0.093\ \ 0.143\ \ 0.028]$ kmol and $Q_0 = 3.37 \times 10^3$ kJ (equivalent to $T_0 = 324.2$ K).

Measurements of $\mathbf{y}(t)$, $q_{ex,j}(t)$, $q_{ex,r}(t)$, $q_{ex,rem}(t)$, $\mathbf{u}_{in}(t)$ and $\omega(t)$ are available with the sampling period $h = 0.4$ s. The measurement errors in $q_{ex,rem}(t)$, $\mathbf{u}_{in}(t)$ and $\omega(t)$ are negligible in comparison to the ones in $\mathbf{y}(t)$, $q_{ex,j}(t)$ and $q_{ex,r}(t)$. The standard deviation of the concentration measurements is 0.5% of the maximum concentration of each species, while the standard deviation of the temperature measurements is 0.5 K. This results in the variance-covariance matrix $\mathbf{\Sigma_y} = \text{diag}\left(\left[65^2\ \ 0.004^2\ \ 0.001^2\ \ 0.001^2\ \ 0.00025^2\right]\right)$.

Two different control objectives are tested:

1. The first objective is to control the numbers of moles $n_\text{A}(t)$ and $n_\text{B}(t)$ to the reference signals $n^s_\text{A}(t)$ and $n^s_\text{B}(t)$, while $Q(t)$ is controlled to the setpoint Q_0, by manipulating the inlet flowrates of the jacket $u_j(t)$, of A $u_{in,\text{A}}(t)$, and of B $u_{in,\text{B}}(t)$. In this case, the reference signals tend exponentially to $1.04n_{\text{A},0}$ and $1.04n_{\text{B},0}$, with a time constant of the exponential convergence of 0.2 min.
2. The second objective is to implement control of temperature and concentration of A, that is, to control the heat $Q(t)$ and the number of moles $n_\text{A}(t)$ to the setpoints Q_0 and $n_{\text{A},0}$, by manipulating the inlet flowrates of the jacket $u_j(t)$ and of A $u_{in,\text{A}}(t)$ to reject a 15 kg min^{-1} step disturbance in the inlet flowrate of B $u_{in,\text{B}}(t)$.

With this information, the following assignments can be made for the controller via feedback linearization in the first case, with the second case being constructed in a similar way:

$$\begin{cases} \mathbf{x}(t) = \begin{bmatrix} Q(t) \\ n_\text{A}(t) \\ n_\text{B}(t) \end{bmatrix}, & \mathbf{y}(t) = \begin{bmatrix} Q(t) \\ \mathbf{n}(t) \end{bmatrix}, \\ \mathbf{F} = \begin{bmatrix} -\Delta\mathbf{H}_r^\text{T} \\ \mathbf{N}_\text{A}^\text{T} \\ \mathbf{N}_\text{B}^\text{T} \end{bmatrix}, & \mathscr{L} = \mathscr{A}, \qquad \mathbf{r}_u\big(\mathbf{x}(t)\big) = \mathbf{r}_v(t), \\ \boldsymbol{\beta}_a\big(\mathbf{y}(t)\big) = \begin{bmatrix} 1 \\ \mathbf{0}_2 \end{bmatrix}\left(q_{ex,rem}(t) - q_{ex,r}(t)\right), & \mathbf{s}_a(t) = \begin{bmatrix} \mathbf{b} & \mathscr{C} \end{bmatrix}\begin{bmatrix} q_{ex}(t) \\ \mathbf{u}_{in}(t) \end{bmatrix} - \omega(t)\mathbf{y}(t), \\ \mathbf{B}_a\big(\mathbf{y}(t)\big) = \begin{bmatrix} 1 & \breve{\mathbf{T}}_{in} \\ 0 & \mathbf{W}_{in,\text{A}} \\ 0 & \mathbf{W}_{in,\text{B}} \end{bmatrix} - \begin{bmatrix} Q(t) \\ n_\text{A}(t) \\ n_\text{B}(t) \end{bmatrix}\begin{bmatrix} 0 & \mathbf{k}_{in}^\text{T} \end{bmatrix}, & \mathbf{u}(t) = \begin{bmatrix} q_{ex,j}(t) \\ \mathbf{u}_{in}(t) \end{bmatrix}, \\ \mathbf{T}_a = \begin{bmatrix} T_{a,Q} & \mathbf{0}_2^\text{T} \\ \mathbf{0}_2 & \mathbf{0}_{2\times 2} \end{bmatrix}, & \bar{\mathbf{u}}(t) = \begin{bmatrix} \bar{q}_{ex,j}(t) \\ \mathbf{u}_{in}(t) \end{bmatrix}. \end{cases} \tag{6.88}$$

Hence, the parameters of the feedback-linearization controller used for this system are mostly determined by readily available information, namely, the stoichiometry, the enthalpies of reaction, the inlet composition and specific heat, and the inlet and outlet flowrates. There is no information about the rate laws.

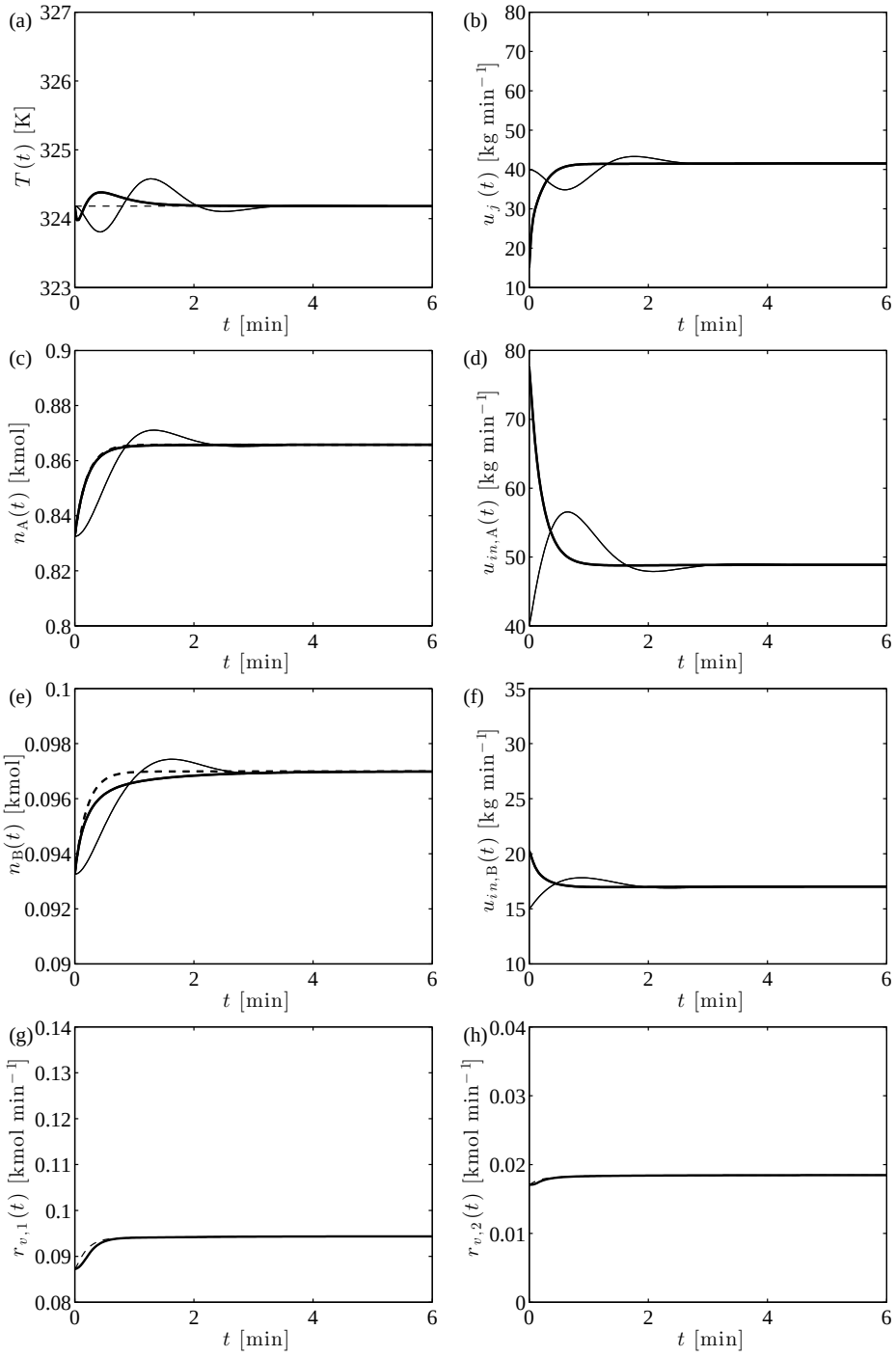

Figure 6.5 – Reference tracking with respect to the numbers of moles of A and B, without measurement noise. (a), (c) and (e): Profiles of temperature and numbers of moles of A and B (controlled variables) for feedback-linearization control (thick line) and PI control (thin line), with the setpoint shown by the dashed line; (b), (d) and (f): Inlet flowrate of the jacket, of A, and of B (manipulated variables); (g) and (h): Estimated (solid lines) and true (dashed lines) reaction rates.

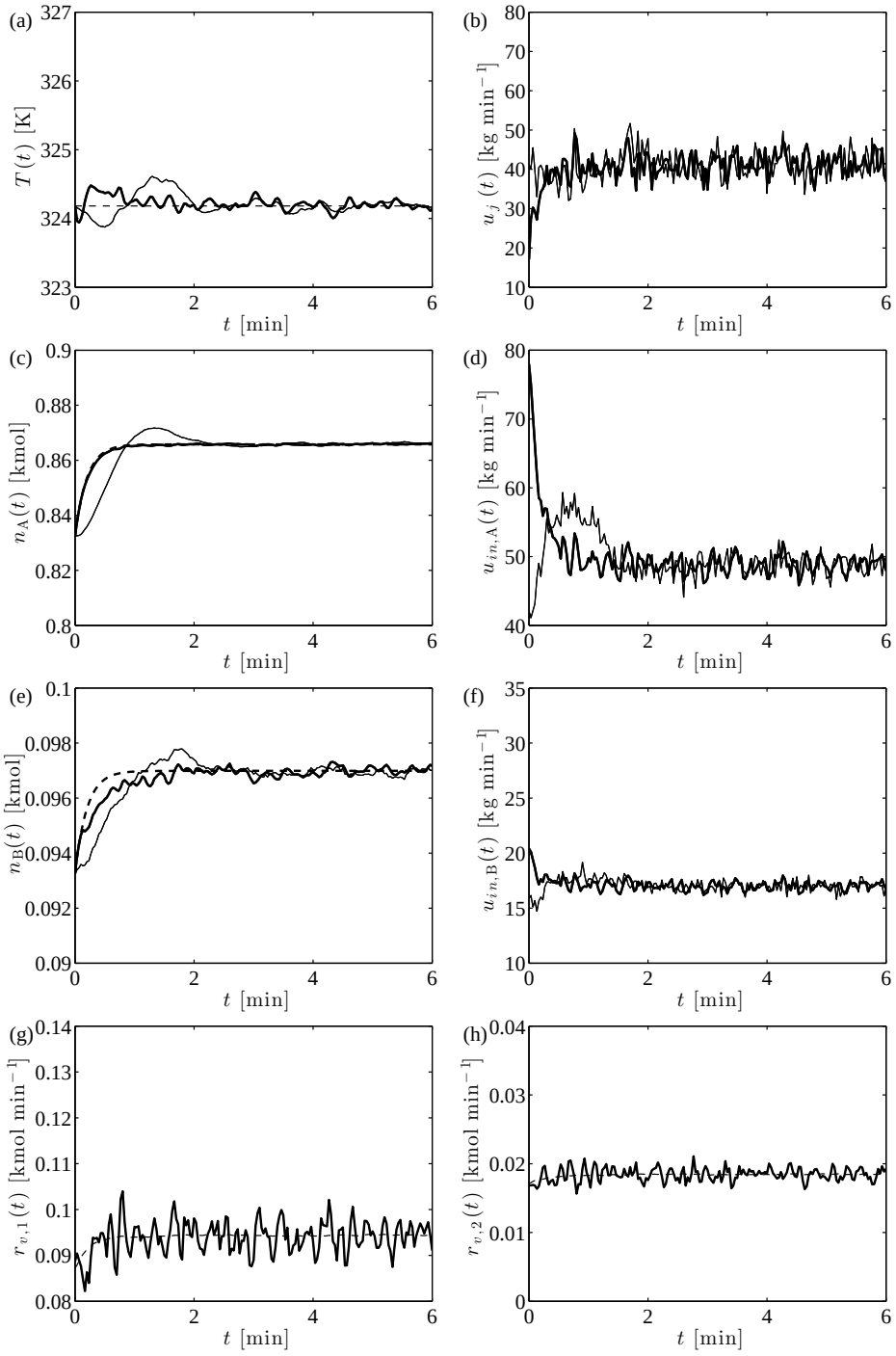

Figure 6.6 – Reference tracking with respect to the numbers of moles of A and B, with measurement noise (standard deviation: 0.5% of the maximum concentration of each species for concentration measurements, 0.5 K for temperature measurements). (a), (c) and (e): Profiles of temperature and numbers of moles of A and B (controlled variables) for feedback-linearization control (thick line) and PI control (thin line), with the setpoint shown by the dashed line; (b), (d) and (f): Inlet flowrate of the jacket, of A, and of B (manipulated variables); (g) and (h): Estimated (solid lines) and true (dashed lines) reaction rates.

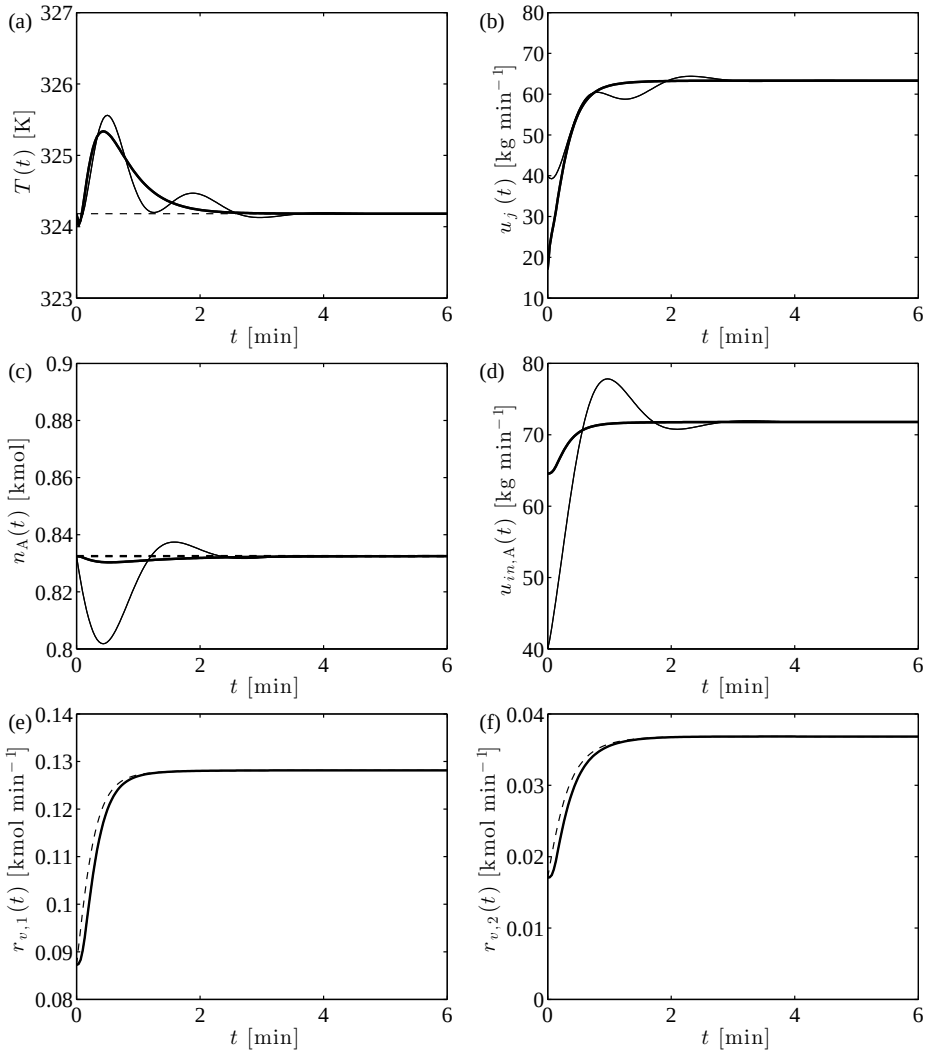

Figure 6.7 – Rejection of a step disturbance in the inlet flowrate of B, without measurement noise. (a) and (c): Profiles of temperature and numbers of moles of A (controlled variables) for feedback-linearization control (thick line) and PI control (thin line), with the setpoint shown by the dashed line; (b) and (d): Inlet flowrate of the jacket and of A (manipulated variables); (e) and (f): Estimated (solid lines) and true (dashed lines) reaction rates.

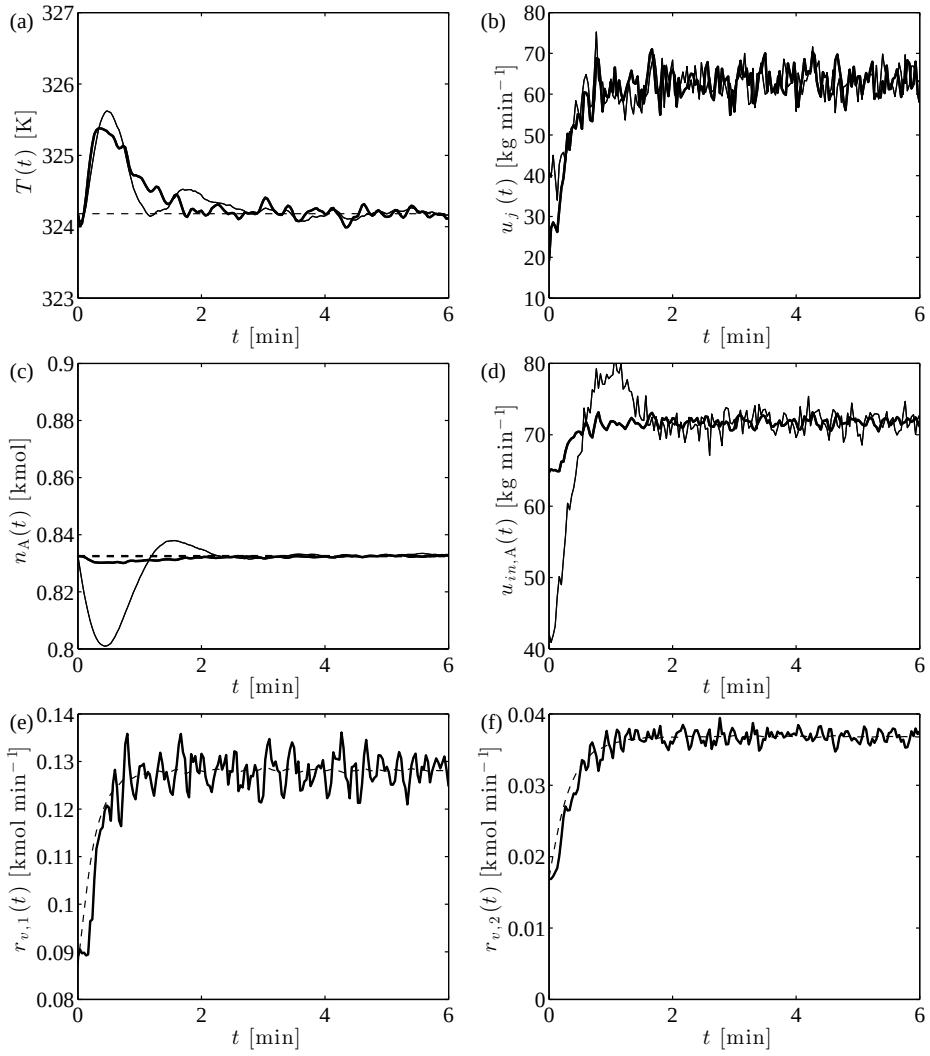

Figure 6.8 – Rejection of a step disturbance in the inlet flowrate of B, with measurement noise (standard deviation: 0.5% of the maximum concentration of each species for concentration measurements, 0.5 K for temperature measurements). (a) and (c): Profiles of temperature and numbers of moles of A (controlled variables) for feedback-linearization control (thick line) and PI control (thin line), with the setpoint shown by the dashed line; (b) and (d): Inlet flowrate of the jacket and of A (manipulated variables); (e) and (f): Estimated (solid lines) and true (dashed lines) reaction rates.

Control via feedback linearization is implemented, using the matrix $\mathbf{\Gamma} = \mathrm{diag}([3\ 1\ 1])$ min^{-1} of exponential convergence rates, the matrix $\mathbf{D} = \mathrm{diag}([0.5\ 0\ 0])$ of desired reduction of the time constants of the actuators, and a differentiation filter of window size $q = 25$ for the estimation of the unknown rates. To simulate the step disturbance of $u_{in,\mathrm{B}}(t)$, the controller output is simply replaced by a constant value.

The feedback-linearization control is compared to the following controllers:

- For temperature control, cascade scheme consisting of PI control in the outer loop with the gain $K_o = 3$ and the integral time constant $T_{i,o} = 0.2$ min and P control in the inner loop with the gain $K_i = -2\ \mathrm{kg}^{-1}\ \mathrm{K}^{-1}\ \mathrm{min}^{-1}$.
- For concentration control of A and B, PI control with the gain $K = 5\ \mathrm{kg}^{-1}\ \mathrm{kmol}^{-1}\ \mathrm{min}^{-1}$ and the integral time constant $T_i = 0.2$ min.

Figures 6.5 and 6.6 show that the feedback-linearization scheme is able to track the reference signals more quickly and precisely than the PI controller, whereas Figures 6.7 and 6.8 show that the feedback-linearization scheme is able to reject the disturbance more quickly than the PI controller. However, if the standard deviation of the concentration measurements is larger than about 1% of the maximum concentration of each species, the estimated reaction rates become too imprecise or delayed (due to the choice of a larger window size q), and the advantage of feedback linearization over PI control is less clear (results not shown).

6.4 Conclusion

This chapter has considered reactor control with and without kinetic models, in both cases using the concept of variants and invariants.

The first part of this chapter has proposed a control scheme via feedback linearization in the presence of a kinetic model. With this control scheme, it has been possible to achieve offset-free control of a subset of the states and set the closed-loop time constants of all the states, for descriptions of the reaction system using either numbers of moles or extents.

The second part of this chapter has considered the control of a subset $\mathbf{x}(t)$ of the available states $\mathbf{y}(t)$ of a generic system. Control is implemented without the knowledge of a rate model and possesses the following main features:

- The controller is mostly based on the structural information about the dynamic relationship between the controlled states $\mathbf{x}(t)$ and the unknown rates $\mathbf{r}_u\big(\mathbf{x}(t)\big)$, the known rates $\boldsymbol{\beta}_a\big(\mathbf{y}(t)\big)$ and the inputs $\mathbf{u}(t)$, and between the available states $\mathbf{y}(t)$ and the unknown rates $\mathbf{r}_u(t)$ and the available rates $\mathbf{s}_a(t)$. This dynamic relationship needs to be known for estimation of the unknown rates.
- Two conditions need to be satisfied: the rank of $\mathbf{B}_a$ must be equal to the number of controlled states n_x and inputs n_u; the rank of $\mathscr{L}$ must be equal to the number of (estimated) unknown rates n_r, which implies that the number of states that are available has to be greater than or equal to n_r. Ideally, the measurements of the available states

and available rates are corrupted by zero-mean noise.

- The controller has three types of tunable parameters with practical meaning, namely: the diagonal matrix $\mathbf{D}$, in which each element of the diagonal specifies the desired reduction of the time constant of each actuator that corresponds to an input in $\mathbf{u}(t)$; the diagonal matrix $\mathbf{\Gamma}$, in which each element of the diagonal corresponds to the inverse of the time constant of the exponential decay of each controlled variable in $\mathbf{x}(t)$; and the parameter of the differentiation filter (the number of samples q in the case of the Savitzky-Golay filter) used for the estimation of the unknown rates $\mathbf{r}_u(t)$. The parameters $\mathbf{D}$, $\mathbf{\Gamma}$ and q need to be chosen to guarantee closed-loop stability, according to their influence on the expected value and variance of $\mathbf{x}(t)$.
- Instead of linearizing the system around a given steady state, this controller implements feedback linearization and uses estimation of unknown rates without knowledge of rate models, which simplifies control design significantly and enables control even when the values of the states are not similar to the corresponding steady-state values. The feedback linearization and the rate estimation set a rate of variation for the controlled variables and allow tracking a trajectory by forcing the control error to decay exponentially to zero.
- The resulting controller is a multiple-input multiple-output (MIMO) controller, which shows good performance for the case of frequent and precise measurements of several output variables. In the case of low measurement noise, feedback linearization coupled to rate estimation can outperform PI control for the purpose of disturbance rejection and setpoint tracking.
- The integral component of a hypothetical PID controller is not needed to eliminate the steady-state error, if it is assumed that all the measurements are corrupted by zero-mean noise, and would only be needed otherwise.
- A simulated example has shown that these conditions are generally satisfied in a realistic control problem, for example, the control of temperature and reactant concentrations in a homogeneous CSTR without kinetic models for the reaction rates, that is, without knowledge of the rate laws.

7 Fast Steady-state Optimization of Dynamic Systems

This chapter is adapted from the postprint of the following article [108]:

D. Rodrigues, M. Amrhein, J. Billeter, and D. Bonvin. Fast estimation of plant steady state for imperfectly known dynamic systems, with application to real-time optimization. *Ind. Eng. Chem. Res.*, 57(10):3699–3716, 2018.

Link: http://doi.org/10.1021/acs.iecr.7b04631.

The author of this thesis contributed to that article by developing the main novel ideas, implementing the simulations, and writing a significant part of the text. Hence, the author retains the right to include the article in this thesis since it is not published commercially and the journal is referenced as the original source.

7.1 Introduction

Kinetic modeling, response-surface modeling and static real-time optimization of continuous processes, among other tasks, require visiting various successive operating points and assessing the steady-state values at these points. It is important to reduce the total amount of time spent by the plant in this exploratory and potentially suboptimal operation, which depends on the number of steady-state evaluations and the time needed for each evaluation. Although a small number of evaluations is often mentioned as a desirable property of the aforementioned applications, less attention has been given to trying to reduce the time needed for each evaluation, which typically requires convergence of the plant to steady state or at least experimental estimation of plant steady state. Note also that, depending on the dominant time constant of the plant, the time necessary to reach steady state may be rather long and represent the main limiting factor. Hence, the objective of this chapter is to investigate methods to speed up the estimation of plant steady state for imperfectly known dynamic systems.

Some contributions have addressed the problem of fast estimation of plant steady state and plant gradients. Typically, this has been done by identifying ARX, ARMAX or Ham-

merstein dynamic models to infer steady-state information from data collected during transient operation [115, 116, 117, 118, 119, 120, 121]. These approaches for dynamic model identification rely on the excitation of the plant, using for example pseudo-random binary sequence signals, and require the collection of many data before the dynamic model can be used to predict the steady-state behavior accurately [122, 123].

One of the main applications that requires the knowledge of plant steady state at successive operating points is the steady-state optimization of continuous processes, often referred to as static real-time optimization (RTO). Static RTO is typically implemented via some iterative scheme that uses steady-state measurements to drive the plant to optimality despite the presence of plant-model mismatch. This mismatch is caused, for example, by an incorrect choice of the model structure, uncertainty associated with parameter estimation, changes in the cost and constraints due to modified economic and operational objectives, or changes in parameters due to changing operating conditions, fouling or the presence of impurities. At each iteration, constant inputs are applied to the plant and, once steady state has been reached, the outputs are measured to evaluate the values of the cost and constraints of the optimization problem. Several RTO approaches have been proposed. The classical strategy is the two-step approach, which, however, may fail to reach plant optimality upon convergence [124, 125]. Hence, other approaches, such as Integrated System Optimization and Parameter Estimation (ISOPE) [126] and Modifier Adaptation (MA) [127, 128], have been developed to enforce the necessary conditions of optimality (NCO) upon convergence. Other approaches, such as Extremum-Seeking Control, Self-Optimizing Control and NCO Tracking, directly adapt the inputs through control schemes that drive the plant toward optimality [129, 130, 131, 132]. In the case of systems with time-scale separation, it has been possible to speed up RTO by treating the slow processes as a source of plant-model mismatch [133]. Furthermore, in the case of parametric plant-model mismatch, it is possible to reach plant optimality in a single transition to steady state by estimating the plant gradients and applying RTO during transient operation [134, 135].

This work proposes a novel way of speeding up the estimation of plant steady state for the case of dynamic systems characterized by fast and slow states. For this to happen, the slow states must not affect the fast states. Furthermore, it is necessary that the uncertain or unknown part of the plant dynamics does not depend on the slow states. Fast estimation of plant steady state is achieved through (i) the use of feedback control to speed up the fast part of the plant, and (ii) the measurement-based estimation of rate signals, which allows computing the steady state of the slow part of the plant. It must be emphasized here that the estimation of rate signals is done *without the knowledge of rate models*, which corresponds to industrial practice with significant plant-model mismatch. In this work, the approach for fast estimation of plant steady state is applied to static RTO, thus enabling what is called *fast static RTO*. The approach is illustrated via the optimization of a continuous stirred-tank reactor (CSTR).

The chapter is organized as follows. Section 7.2 presents the dynamic model of the class of systems considered in this chapter. Section 7.3 shows how to implement measurement-

based rate estimation without a rate model. Then, Section 7.4 describes how rate estimation can be used to implement fast estimation of plant steady state by (i) speeding up the response of the fast part via feedback control, and (ii) using the estimated rates to compute the steady state of the slow part during transient operation. The implementation of fast estimation of plant steady state is illustrated on a simulated CSTR. Section 7.5 describes how the fast estimation of plant steady state can be used in the context of static RTO. Its implementation is illustrated on the same simulated CSTR. Finally, Section 7.6 concludes the chapter.

7.2 System Description

This section describes the general features of the systems for which fast estimation of plant steady state will be proposed in this chapter.

7.2.1 Dynamic model with fast and slow states

Let us consider a time-invariant nonlinear dynamic system with the input vector $\mathbf{u}(t)$ of dimension n_u. This system consists of two subsystems with the states $\mathbf{x}(t)$ of dimension n_x and the states $\mathbf{z}(t)$ of dimension n_z:

$$\dot{\mathbf{x}}(t) = \mathbf{f}\big(\mathbf{x}(t), \mathbf{u}(t)\big), \qquad \mathbf{x}(0) = \mathbf{x}_0, \tag{7.1}$$

$$\dot{\mathbf{z}}(t) = \mathbf{h}\big(\mathbf{x}(t), \mathbf{z}(t), \mathbf{u}(t)\big), \qquad \mathbf{z}(0) = \mathbf{z}_0, \tag{7.2}$$

where $\mathbf{f}(\mathbf{x}, \mathbf{u})$ and $\mathbf{h}(\mathbf{x}, \mathbf{z}, \mathbf{u})$ are bounded.

As can be seen from Eqs. (7.1)–(7.2), a particularity of this system is the following fact:

Assumption 7.1. *The states $\mathbf{z}(t)$ do not affect the states $\mathbf{x}(t)$. As a consequence, $\mathbf{x}(t)$ and $\mathbf{z}(t)$ correspond to fast and slow dynamics, respectively.*

Indeed, since $\mathbf{z}(t)$ do not affect $\mathbf{x}(t)$, steady state for $\mathbf{x}$ only requires that $\mathbf{u}$ be at steady state. However, steady state for $\mathbf{z}$ requires that both $\mathbf{u}$ and $\mathbf{x}$ be at steady state. Hence, $\mathbf{u}$ and $\mathbf{x}$ may be at steady state, with $\mathbf{z}$ still in transient mode.

Another particularity of this system, which will be considered throughout this chapter, is that a part of its dynamics is unknown and satisfies the following assumption:

Assumption 7.2. *The unknown part of the dynamics depends only on the fast states $\mathbf{x}(t)$.*

Consequently, let us introduce the following notations without any additional assumption:

- The vector field $\mathbf{f}(\mathbf{x}, \mathbf{u})$ is expressed as the sum $\mathbf{f}(\mathbf{x}, \mathbf{u}) := \mathbf{f}_u(\mathbf{x}, \mathbf{u}) + \mathbf{f}_a(\mathbf{x}, \mathbf{u})$, where the subscripts $(\cdot)_u$ and $(\cdot)_a$ indicate unknown and known (available) functions, respectively. Similarly, the vector field $\mathbf{h}(\mathbf{x}, \mathbf{z}, \mathbf{u})$ is expressed as the sum of unknown and known parts, $\mathbf{h}(\mathbf{x}, \mathbf{z}, \mathbf{u}) := \mathbf{h}_u(\mathbf{x}, \mathbf{u}) + \mathbf{h}_a(\mathbf{x}, \mathbf{z}, \mathbf{u})$.
- The vector field $\mathbf{h}_u(\mathbf{x}, \mathbf{u})$ is expressed as known linear combinations of the n_r un-

known rate functions $\mathbf{r}_u(\mathbf{x},\mathbf{u})$, that is, $\mathbf{h}_u(\mathbf{x},\mathbf{u}) := \mathbf{H}\,\mathbf{r}_u(\mathbf{x},\mathbf{u})$, with $\mathbf{H}$ a known $(n_z \times n_r)$-dimensional matrix. The vector field $\mathbf{f}_u(\mathbf{x},\mathbf{u})$ can be expressed as known linear combinations of the same unknown rate functions $\mathbf{r}_u(\mathbf{x},\mathbf{u})$ plus the additional term $\mathbf{s}_u(\mathbf{x},\mathbf{u})$, that is, $\mathbf{f}_u(\mathbf{x},\mathbf{u}) := \mathbf{F}\,\mathbf{r}_u(\mathbf{x},\mathbf{u}) + \mathbf{s}_u(\mathbf{x},\mathbf{u})$, with $\mathbf{F}$ a known $(n_x \times n_r)$-dimensional matrix.

Note that Assumption 7.2 implies that (i) the functions $\mathbf{s}_u(\mathbf{x},\mathbf{u})$ and $\mathbf{r}_u(\mathbf{x},\mathbf{u})$ are unknown but independent of the slow states $\mathbf{z}$, and (ii) the known functions $\mathbf{f}_a(\mathbf{x},\mathbf{u})$ and $\mathbf{h}_a\big(\mathbf{x},\mathbf{z},\mathbf{u}\big)$ allow computing the values $\mathbf{f}_a(t)$ and $\mathbf{h}_a(t)$ from knowledge of $\mathbf{x}(t)$, $\mathbf{z}(t)$ and $\mathbf{u}(t)$.

In continuous processes, the system moves from one steady state to the next following changes in the inputs. Let us consider the fast subsystem at the $(k-1)$st steady state $\bar{\mathbf{x}}_{k-1}$, that is, $\mathbf{x}(t_{k-1}) = \bar{\mathbf{x}}_{k-1}$. With Assumptions 7.1 and 7.2, and the notations presented above, the system dynamics read:

$$\dot{\mathbf{x}}(t) = \mathbf{F}\,\mathbf{r}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big) + \mathbf{s}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big) + \mathbf{f}_a\big(\mathbf{x}(t),\mathbf{u}(t)\big), \quad \mathbf{x}(t_{k-1}) = \bar{\mathbf{x}}_{k-1}, \tag{7.3}$$

$$\dot{\mathbf{z}}(t) = \mathbf{H}\,\mathbf{r}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big) + \mathbf{h}_a\big(\mathbf{x}(t),\mathbf{z}(t),\mathbf{u}(t)\big), \quad \mathbf{z}(t_{k-1}) = \mathbf{z}_{k-1}, \tag{7.4}$$

where $\bar{(\cdot)}$ denotes a steady-state value, which means that $(\bar{\mathbf{x}}_{k-1},\bar{\mathbf{z}}_{k-1})$ is the steady state that corresponds to the inputs $\bar{\mathbf{u}}_{k-1}$. Note that the slow states $\mathbf{z}(t_{k-1})$ are not necessarily at steady state yet, and the initial condition $\mathbf{z}_{k-1}$ may be different from the steady-state values $\bar{\mathbf{z}}_{k-1}$. If, at time t_{k-1}, the inputs are changed to new values, the system will reach a new steady state with the inputs $\bar{\mathbf{u}}_k$ and the states $\bar{\mathbf{x}}_k$ and $\bar{\mathbf{z}}_k$. The outputs $\mathbf{y}(t)$ of dimension n_y are expressed as linear combinations of the states, that is,

$$\mathbf{y}(t) = \mathbf{C}_x\,\mathbf{x}(t) + \mathbf{C}_z\,\mathbf{z}(t), \tag{7.5}$$

and are available as $\tilde{\mathbf{y}}(t)$, where $\tilde{(\cdot)}$ denotes noisy measurements.

Furthermore, we will consider the following assumption throughout the chapter:

Assumption 7.3. *The eigenvalues of* $\frac{\partial \mathbf{h}_a}{\partial \mathbf{z}}(\mathbf{x},\mathbf{z},\mathbf{u})$ *have strictly negative real parts. This implies that (i)* $\frac{\partial \mathbf{h}_a}{\partial \mathbf{z}}\big(\mathbf{x},\mathbf{z},\mathbf{u}\big)$ *is invertible, and (ii)* $\mathbf{z}(t)$ *is open-loop stable since* $\mathbf{h}_u(\mathbf{x},\mathbf{u})$ *is bounded.*

7.2.2 Example: Fast and slow states in a CSTR

As an example of the system given by Eqs. (7.3)–(7.4), a homogeneous CSTR with S species, R independent reactions, p inlet streams and one outlet stream is considered next. The volume V and the density ρ are assumed to be constant, and the specific heat capacity c_p is assumed to depend only on temperature. The S species are separated into two groups:

1. S_P species that are not fed to the reactor and whose concentrations have no effect on the reaction rates. The corresponding vector of numbers of moles is represented by $\mathbf{n}_P$ (mostly products);
2. $S_R = S - S_P$ remaining species that are fed to the reactor or whose concentrations influence the reaction rates. The corresponding vector of numbers of moles is represented by $\mathbf{n}_R$ (mostly reactants). Among these S_R species, S_F species are fed to the reactor,

with $S_F \leq p$, while $S_I = S_R - S_F$ species are not fed. It is also assumed that, for S_F inlet streams, each of them is composed of a single species and possibly solvents (with the inlet mass fractions of these species specified by the $S_F \times S_F$ diagonal matrix $\check{\mathbf{W}}_{in,F}$), and the remaining $(p - S_F)$ inlet streams contain only solvents.

Furthermore, let $Q := V\rho\bar{c}_p(T - T_{ref})$ denote the heat of the reaction mixture, with T being the reactor temperature, T_{ref} the reference temperature and $\bar{c}_p$ the average specific heat capacity between T and T_{ref}, and assume that the inlets are at the temperature T_{ref}.

The heat and mole balances can be written as:

$$\begin{bmatrix} \dot{Q}(t) \\ \dot{\mathbf{n}}_R(t) \\ \dot{\mathbf{n}}_P(t) \end{bmatrix} = \begin{bmatrix} -\boldsymbol{\Delta}\mathbf{H}_r^{\mathrm{T}} \\ \mathbf{N}_R^{\mathrm{T}} \\ \mathbf{N}_P^{\mathrm{T}} \end{bmatrix} V\,\boldsymbol{\varphi}\left(Q(t), \mathbf{n}_R(t)\right) + \begin{bmatrix} 1 & \mathbf{0}_p^{\mathrm{T}} \\ \mathbf{0}_{S_R} & \mathbf{W}_{in,R} \\ \mathbf{0}_{S_P} & \mathbf{0}_{S_P \times p} \end{bmatrix} \begin{bmatrix} q_{ex}(t) \\ \mathbf{u}_{in}(t) \end{bmatrix} - \omega(t) \begin{bmatrix} Q(t) \\ \mathbf{n}_R(t) \\ \mathbf{n}_P(t) \end{bmatrix}, \tag{7.6}$$

which shows that $Q(t)$ and $\mathbf{n}_R(t)$ are fast states and $\mathbf{n}_P(t)$ are slow states since $\mathbf{n}_P(t)$ do not affect the dynamics of the remaining states. In Eq. (7.6), $\boldsymbol{\Delta}\mathbf{H}_r$ are the enthalpies of reaction, $\mathbf{N}_R$ and $\mathbf{N}_P$ the stoichiometric submatrices involving the reactants and the products, respectively, $\boldsymbol{\varphi}\left(Q(t), \mathbf{n}_R(t)\right)$ the R reaction rates expressed as functions of the fast states, $q_{ex}(t)$ the heat exchange power, $\mathbf{u}_{in}(t)$ the p inlet flowrates, $\omega(t) := \mathbf{k}_{in}^{\mathrm{T}}\mathbf{u}_{in}(t)$ the inverse of the residence time, with $\mathbf{k}_{in} := \frac{\mathbf{1}_p}{\rho V}$, and

$$\mathbf{W}_{in,R} := \mathbf{M}_{w,R}^{-1} \begin{bmatrix} \check{\mathbf{W}}_{in,F} & \mathbf{0}_{S_F \times (p - S_F)} \\ \mathbf{0}_{S_I \times S_F} & \mathbf{0}_{S_I \times (p - S_F)} \end{bmatrix}, \tag{7.7}$$

with $\mathbf{M}_{w,R}$ the diagonal matrix of molecular weights of the reactants. The stoichiometric submatrices $\mathbf{N}_R$ and $\mathbf{N}_P$ are constant and can be determined via target factor analysis [20]. Note that, owing to the definition of the heat Q, the enthalpies of reaction $\boldsymbol{\Delta}\mathbf{H}_r$ are constant and not temperature dependent since they correspond to the enthalpies at the reference temperature T_{ref}, and not at the reactor temperature T. Moreover, these enthalpies are also known since they can be computed as $\boldsymbol{\Delta}\mathbf{H}_r = \mathbf{N}_R\boldsymbol{\Delta}\mathbf{H}_R + \mathbf{N}_P\boldsymbol{\Delta}\mathbf{H}_P$, where $\boldsymbol{\Delta}\mathbf{H}_R$ and $\boldsymbol{\Delta}\mathbf{H}_P$ are the enthalpies of formation of the reactants and products at T_{ref}. More details about the notation can be found in Section 2.2.

It is possible to write Model (7.6) in the general form given by Eqs. (7.3)–(7.4) by assigning

$$\mathbf{x}(t) := \begin{bmatrix} Q(t) \\ \mathbf{n}_R(t) \end{bmatrix}, \qquad \mathbf{z}(t) := \mathbf{n}_P(t), \qquad \mathbf{u}(t) := \begin{bmatrix} q_{ex}(t) \\ \mathbf{u}_{in}(t) \end{bmatrix}, \tag{7.8a}$$

$$\mathbf{r}_u\big(\mathbf{x}(t)\big) := \mathbf{r}_v(t), \qquad \mathbf{s}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big) := \mathbf{0}_{S_R+1}, \tag{7.8b}$$

$$\mathbf{f}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big) := \begin{bmatrix} -\boldsymbol{\Delta}\mathbf{H}_r^{\mathrm{T}} \\ \mathbf{N}_R^{\mathrm{T}} \end{bmatrix} \mathbf{r}_v(t), \qquad \mathbf{F} := \begin{bmatrix} -\boldsymbol{\Delta}\mathbf{H}_r^{\mathrm{T}} \\ \mathbf{N}_R^{\mathrm{T}} \end{bmatrix}, \tag{7.8c}$$

$$\mathbf{f}_a\big(\mathbf{x}(t),\mathbf{u}(t)\big) := \begin{bmatrix} \mathbf{b} & \mathscr{C} \end{bmatrix} \begin{bmatrix} q_{ex}(t) \\ \mathbf{u}_{in}(t) \end{bmatrix} - \begin{bmatrix} Q(t) \\ \mathbf{n}_R(t) \end{bmatrix} \begin{bmatrix} 0 & \mathbf{k}_{in}^{\mathrm{T}} \end{bmatrix} \begin{bmatrix} q_{ex}(t) \\ \mathbf{u}_{in}(t) \end{bmatrix}, \tag{7.8d}$$

$$\mathbf{h}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big) := \mathbf{N}_P^{\mathrm{T}}\,\mathbf{r}_v(t), \qquad \mathbf{H} := \mathbf{N}_P^{\mathrm{T}}, \tag{7.8e}$$

$$\mathbf{h}_a\big(\mathbf{z}(t),\mathbf{u}(t)\big) := -\mathbf{k}_{in}^{\mathrm{T}}\mathbf{u}_{in}(t)\mathbf{n}_P(t), \tag{7.8f}$$

with

$$\mathbf{r}_v(t) := V\,\boldsymbol{\varphi}\big(Q(t),\mathbf{n}_R(t)\big), \qquad \mathbf{b} := \begin{bmatrix} 1 \\ \mathbf{0}_{S_R} \end{bmatrix}, \qquad \mathscr{C} := \begin{bmatrix} \mathbf{0}_p^{\mathrm{T}} \\ \mathbf{W}_{in,R} \end{bmatrix}. \tag{7.8g}$$

Note that the assumptions in this example are realistic for many reaction systems. Indeed, it is often known that the reaction rates are not affected by the concentrations of some products (in particular, if the reactions are elementary, but not if they are autocatalytic or product-inhibited), which implies that these concentrations are part of the slow states $\mathbf{z}$. On the other hand, since the product concentrations enter the formulation of many optimization problems, it is beneficial to estimate their steady-state values as quickly as possible.

7.3 Measurement-based Rate Estimation

A measurement-based rate estimation method is developed next to estimate the rates $\mathbf{r}_u(t)$ from the inputs and the noisy output measurements. This method is similar to the one presented in Chapter 5. For the kth iteration, as soon as the states $\mathbf{x}(t)$ and the inputs $\mathbf{u}(t)$ converge to the steady-state values $\bar{\mathbf{x}}_k$ and $\bar{\mathbf{u}}_k$, this rate estimation yields the steady-state values $\hat{\bar{\mathbf{r}}}_{u,k}$. Note that this rate estimation is nonparametric and *does not rely on rate models*. The feasibility of this rate estimation method depends on the additional assumptions that are made regarding the structure of the dynamic model and the available outputs, as shown next.

7.3.1 Relationship between unknown rates and outputs

The aim is to estimate the unknown rates $\mathbf{r}_u(t)$ from available signals, in this case the inputs $\mathbf{u}(t)$ and the measured outputs $\tilde{\mathbf{y}}(t)$. For this, we will introduce a few additional

assumptions to be able to express Eqs. (7.3)–(7.5) as a dynamic model for the outputs $\mathbf{y}(t)$ where the rates $\mathbf{r}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big)$ are the only unknown part.

Assumption 7.4. *$\mathbf{C}_x$ and $\mathbf{C}_z$ are such that $\mathbf{C}_x\,\mathbf{f}_a\big(\mathbf{x}(t),\mathbf{u}(t)\big)+\mathbf{C}_z\,\mathbf{h}_a\big(\mathbf{x}(t),\mathbf{z}(t),\mathbf{u}(t)\big)$ can be computed as known functions of the inputs $\mathbf{u}(t)$ and the outputs $\mathbf{y}(t)$, that is, $\mathbf{s}_a\big(\mathbf{y}(t),\mathbf{u}(t)\big):=\mathbf{C}_x\,\mathbf{f}_a\big(\mathbf{x}(t),\mathbf{u}(t)\big)+\mathbf{C}_z\,\mathbf{h}_a\big(\mathbf{x}(t),\mathbf{z}(t),\mathbf{u}(t)\big)$.*

Assumption 7.5. *$\mathbf{C}_x$ is such that the unknown functions $\mathbf{s}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big)$ are not sensed by the outputs, that is, $\mathbf{C}_x\,\mathbf{s}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big)=\mathbf{0}_{n_y}$.*

From Eqs. (7.3)–(7.5) and Assumptions 7.4 and 7.5, the dynamics of the outputs $\mathbf{y}(t)$ read:

$$\dot{\mathbf{y}}(t)=\mathscr{L}\,\mathbf{r}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big)+\mathbf{s}_a\big(\mathbf{y}(t),\mathbf{u}(t)\big),\qquad \mathbf{y}(0)=\mathbf{C}_x\,\mathbf{x}_0+\mathbf{C}_z\,\mathbf{z}_0, \tag{7.9}$$

with $\mathscr{L}:=\mathbf{C}_x\,\mathbf{F}+\mathbf{C}_z\,\mathbf{H}$. Hence, $\mathbf{r}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big)$ is the only unknown part in Eq. (7.9) and can be estimated by solving Eq. (7.9), provided that the matrix $\mathscr{L}$ has full column rank, as expressed by the following assumption:

Assumption 7.6. *$\mathscr{L}$ is a known $(n_y\times n_r)$-dimensional matrix with* $\operatorname{rank}(\mathscr{L})=n_r$.

The following proposition shows how the rates $\mathbf{r}_u(t)$ can be estimated to yield the estimates $\hat{\mathbf{r}}_u(t)$ and the corresponding steady-state values $\hat{\bar{\mathbf{r}}}_{u,k}$.

Proposition 7.1. *Let the states $\mathbf{x}(t)$ and $\mathbf{z}(t)$ and the outputs $\mathbf{y}(t)$ be described by Eqs.* (7.3)–(7.5) *and Assumptions 7.4–7.6 hold, which implies that $\mathbf{y}(t)$ evolve dynamically as shown in Eq.* (7.9).

Then, the estimates $\hat{\mathbf{r}}_u(t)$ can be computed from the inputs $\mathbf{u}(t)$, the measurements $\tilde{\mathbf{y}}(t)$, and the estimated derivatives $\hat{\dot{\mathbf{y}}}(t)$, as follows:

$$\hat{\mathbf{r}}_u(t)=\mathscr{T}\Big(\hat{\dot{\mathbf{y}}}(t)-\mathbf{s}_a\big(\tilde{\mathbf{y}}(t),\mathbf{u}(t)\big)\Big), \tag{7.10}$$

where the $(n_r\times n_y)$-dimensional matrix $\mathscr{T}$ is such that $\mathscr{T}\mathscr{L}=\mathbf{I}_{n_r}$.

The steady-state rates $\hat{\bar{\mathbf{r}}}_{u,k}$ can then be computed as:

$$\hat{\bar{\mathbf{r}}}_{u,k}=\mathscr{T}\Big(\hat{\dot{\mathbf{y}}}(t_k)-\mathbf{s}_a\big(\mathbf{C}_x\,\bar{\mathbf{x}}_k+\mathbf{C}_z\,\tilde{\mathbf{z}}(t_k),\bar{\mathbf{u}}_k\big)\Big). \tag{7.11}$$

Proof. Applying the linear transformation specified by the matrix $\mathscr{T}$ to Eq. (7.9) yields Eq. (7.10). Since $\mathbf{y}(t_k)=\mathbf{C}_x\,\bar{\mathbf{x}}_k+\mathbf{C}_z\,\mathbf{z}(t_k)$ when the steady state $\bar{\mathbf{x}}_k$ is reached at the time instant t_k, one can obtain Eq. (7.11). □

In particular, let us suppose that (i) the outputs $\mathbf{y}(t)$ are all the fast states $\mathbf{x}(t)$, which guarantees Assumption 7.4, (ii) $\mathbf{s}_u(\mathbf{x},\mathbf{u})=\mathbf{0}_{n_x}$, which guarantees Assumption 7.5, and (iii) $\mathbf{F}$ is a known $(n_x\times n_r)$-dimensional matrix with $\operatorname{rank}(\mathbf{F})=n_r$, which guarantees Assumption 7.6. Note that these conditions are typically satisfied in the CSTR example shown above.

Then, the estimates $\hat{\mathbf{r}}_u(t)$ can be computed from the inputs $\mathbf{u}(t)$, the measurements $\tilde{\mathbf{x}}(t)$, and the estimated derivatives $\dot{\tilde{\mathbf{x}}}(t)$, as follows:

$$\hat{\mathbf{r}}_u(t) = \mathscr{T}\left(\dot{\tilde{\mathbf{x}}}(t) - \mathbf{f}_a\big(\tilde{\mathbf{x}}(t), \mathbf{u}(t)\big)\right), \tag{7.12}$$

where the $(n_r \times n_x)$-dimensional matrix $\mathscr{T}$ is such that $\mathscr{T}\mathbf{F} = \mathbf{I}_{n_r}$.

The steady-state rates $\hat{\bar{\mathbf{r}}}_{u,k}$ can then be computed as:

$$\hat{\bar{\mathbf{r}}}_{u,k} = \mathscr{T}\big(\dot{\bar{\mathbf{x}}}(t_k) - \mathbf{f}_a(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k)\big). \tag{7.13}$$

7.3.2 Rate estimator based on convolution filters

One can use a convolution filter to estimate the rates $\hat{\mathbf{r}}_u(t)$ from the measurements $\tilde{\mathbf{y}}(t)$ and the rates $\tilde{\mathbf{s}}_a(t)$, with $\tilde{\mathbf{s}}_a(t)$ computed from the known functions $\mathbf{s}_a(\mathbf{y}, \mathbf{u})$, the inputs $\mathbf{u}(t)$, and the measurements $\tilde{\mathbf{y}}(t)$. Note that $\mathbf{r}_u\big(\mathbf{x}(t), \mathbf{u}(t)\big)$ becomes constant upon convergence of $\mathbf{x}(t)$ and $\mathbf{u}(t)$ to $\bar{\mathbf{x}}_k$ and $\bar{\mathbf{u}}_k$. For the sake of simplicity, the functions $\mathbf{r}_u$ and $\mathbf{s}_a$ are written as time-variant signals in the remainder of this section.

Let us recall the concept of variants, which have been formulated and used for rate estimation in a generic sense in Chapter 5. Given a set of n_r unknown rates, the variants are also of dimension n_r, with each variant depending on only one unknown rate and containing all the information about that rate. As such, a variant is decoupled from all the other unknown rates. The concept of reaction variants for homogeneous reactors is a well-known example of variants [12]. Hence, upon defining the states $\mathbf{y}_r(t) := \mathscr{T}\,\mathbf{y}(t)$, Eq. (7.9) results in:

$$\dot{\mathbf{y}}_r(t) = \mathbf{r}_u(t) + \mathscr{T}\,\mathbf{s}_a(t), \tag{7.14}$$

which implies that $\mathbf{y}_r(t)$ are variants. Then, the rate estimates $\hat{\mathbf{r}}_u(t)$ can be computed as:

$$\hat{\mathbf{r}}_u(t) = \dot{\tilde{\mathbf{y}}}_r(t) - \mathscr{T}\,\tilde{\mathbf{s}}_a(t), \tag{7.15}$$

which indicates that differentiation needs to be applied to $\tilde{\mathbf{y}}_r$. The differentiating convolution filter presented in Section 5.4.1 can be used for this purpose.

In particular, when $\mathbf{r}_u$ reaches steady state, Assumption 5.1 is verified, the results in Proposition 5.2 also hold for the *steady-state* rate estimates $\hat{\bar{\mathbf{r}}}_{u,k}$ by substituting t with t_k, and $\hat{\bar{\mathbf{r}}}_{u,k}$ can be computed without bias from $\tilde{\mathbf{y}}_r$ and $\tilde{\mathbf{s}}_a$ in the interval $\left[t_k - \Delta t, t_k\right]$ as:

$$\hat{\bar{\mathbf{r}}}_{u,k} = \sum_{k=0}^{q-1} \frac{c_{k+1}}{h}\,\tilde{\mathbf{y}}_r(t_k - \Delta t + kh) - \left(\sum_{k=0}^{q-1} b_{k+1}\mathscr{T}\,\tilde{\mathbf{s}}_a(t_k - \Delta t + kh)\right). \tag{7.16}$$

7.4 Fast Estimation of Plant Steady State

The concept of measurement-based rate estimation without a rate model is used in this section to speed up the estimation of plant steady state. This is done in two steps: (i) feedback control is applied to speed up the convergence of the fast states $\mathbf{x}$ to steady state, and (ii) estimation of the steady state of $\mathbf{z}$ is performed as soon as the fast states $\mathbf{x}$ reach steady state, that is, still during the transient of the slow states.

7.4.1 Speeding up $\mathbf{x}(t)$ via feedback control

Assuming that the fast states $\mathbf{x}$ are accessible, their steady state $\bar{\mathbf{x}}_k$ can typically be reached faster via the use of feedback control. For this, the states $\mathbf{x}$ are the controlled variables (CVs), $\mathbf{x}^s$ are the setpoints, while the inputs $\mathbf{u}$ are the manipulated variables (MVs) that also converge to $\bar{\mathbf{u}}_k$ at steady state.

7.4.1.1 Response speed

We provide a way of assessing how much time can be saved by enforcing steady state faster for $\mathbf{x}$ via feedback control. This quantitative assessment uses the concept of eigenvalues (or time constants). For this, the slow system in Eq. (7.2) need not be considered since the states $\mathbf{z}$ do not affect $\mathbf{x}$. The fast system in Eq. (7.1) is linearized around the steady-state values $\bar{\mathbf{x}}_{k-1}$ and $\bar{\mathbf{u}}_{k-1}$:

$$\delta\dot{\mathbf{x}}(t) = \mathbf{A}\delta\mathbf{x}(t) + \mathbf{B}\delta\mathbf{u}(t), \qquad \delta\mathbf{x}(t_{k-1}) = \mathbf{0}, \tag{7.17}$$

where $\delta\mathbf{x}(t) := \mathbf{x}(t) - \bar{\mathbf{x}}_{k-1}$, $\delta\mathbf{u}(t) := \mathbf{u}(t) - \bar{\mathbf{u}}_{k-1}$, $\mathbf{A} := \frac{\partial \mathbf{f}}{\partial \mathbf{x}}(\bar{\mathbf{x}}_{k-1}, \bar{\mathbf{u}}_{k-1})$, $\mathbf{B} := \frac{\partial \mathbf{f}}{\partial \mathbf{u}}(\bar{\mathbf{x}}_{k-1}, \bar{\mathbf{u}}_{k-1})$.

In the absence of feedback control, the response speed is given by the eigenvalues of $\mathbf{A}$. On the other hand, if one considers proportional control with the gain matrix $\mathbf{K}$, the dominant time constant can be reduced since it is linked to the eigenvalues of $(\mathbf{A} - \mathbf{BK})$.

7.4.1.2 Control via feedback linearization

One could use multivariable control such as pole placement or optimal control [136]. However, these approaches require a dynamic process model, which is assumed to be lacking in this study. Alternatively, one can take advantage of the rate estimates and use the control approach that relies on rate estimation and input-output feedback linearization presented in Section 6.3, as shown next.

Feedback control is needed to drive the fast states $\mathbf{x}(t)$ as quickly as possible to the steady-state setpoints $\bar{\mathbf{x}}^s$. On the other hand, the inputs $\mathbf{u}(t)$ should have low sensitivity with respect to measurement noise, in particular when the steady state $\bar{\mathbf{x}}$ is reached, because $\bar{\mathbf{u}}$ and $\bar{\mathbf{x}}$ are used jointly to estimate the plant steady state. The control scheme via feedback linearization described next is quite appropriate to achieve these two goals.

Let us consider Eq. (7.3) with (i) $\mathbf{s}_u(\mathbf{x},\mathbf{u}) = \mathbf{0}_{n_x}$, (ii) $\mathbf{f}_a$ affine in $\mathbf{u}$, namely $\mathbf{f}_a(\mathbf{x},\mathbf{u}) := \boldsymbol{\beta}_a(\mathbf{x}) + \mathbf{B}_a(\mathbf{x})\,\mathbf{u}$, and (iii) $\mathbf{r}_u$ independent of $\mathbf{u}$. With these additional assumptions, Eq. (7.3) becomes:

$$\dot{\mathbf{x}}(t) = \mathbf{F}\,\mathbf{r}_u\big(\mathbf{x}(t)\big) + \boldsymbol{\beta}_a\big(\mathbf{x}(t)\big) + \mathbf{B}_a\big(\mathbf{x}(t)\big)\,\mathbf{u}(t). \tag{7.18}$$

Furthermore, let $n_x = n_u$ and $\mathbf{B}_a\big(\mathbf{x}(t)\big)$ be invertible. Introducing the new inputs $\mathbf{v}(t)$ to represent the right-hand side of Eq. (7.18) results in the following feedback linearization law:

$$\mathbf{u}(t) = \mathbf{B}_a\big(\tilde{\mathbf{x}}(t)\big)^{-1}\Big(\mathbf{v}(t) - \mathbf{F}\,\hat{\mathbf{r}}_u(t) - \boldsymbol{\beta}_a\big(\tilde{\mathbf{x}}(t)\big)\Big). \tag{7.19}$$

One can design a feedback controller that forces the control error $\mathbf{e}(t) := \mathbf{x}^s(t) - \mathbf{x}(t)$ to converge exponentially to zero at the rates specified by the diagonal matrix $\boldsymbol{\Gamma}$, that is, $\dot{\mathbf{e}}(t) = -\boldsymbol{\Gamma}\,\mathbf{e}(t)$. This can be obtained when $\dot{\mathbf{x}}(t) = \mathbf{v}(t)$ by using the control law

$$\mathbf{v}(t) = \dot{\mathbf{x}}^s(t) + \boldsymbol{\Gamma}\,\big(\mathbf{x}^s(t) - \tilde{\mathbf{x}}(t)\big). \tag{7.20}$$

Note that the control law in Eq. (7.20) uses $\dot{\mathbf{x}}^s(t)$, which ideally requires prior knowledge of the setpoints $\mathbf{x}^s(t)$. To avoid very large derivatives, the setpoints can be forced to obey the dynamic relationships

$$\dot{\mathbf{x}}^s(t) = \alpha\,\big(\bar{\mathbf{x}}^s - \mathbf{x}^s(t)\big). \tag{7.21}$$

This way, with the control laws in Eqs. (7.20)–(7.21), the states $\mathbf{x}(t)$ can be driven quickly, with the dominant time constant α^{-1}, to the steady states $\bar{\mathbf{x}}^s$, and this *independently of the controller gains* $\boldsymbol{\Gamma}$.

However, note that the key relationship $\dot{\mathbf{x}}(t) = \mathbf{v}(t)$ holds only if the error between the estimated values $\hat{\mathbf{r}}_u(t)$ and the true values $\mathbf{r}_u\big(\mathbf{x}(t)\big)$ is negligible. In practice, according to Appendix D.3, there will be a bias between the estimated values $\hat{\mathbf{r}}_u(t)$ and the true values $\mathbf{r}_u\big(\mathbf{x}(t)\big)$ before steady state is reached. This estimation bias acts as a disturbance that affects the control error. By expressing $\mathbf{v}(t)$ in Eq. (7.19) from Eq. (7.20) and using the resulting equation to express $\mathbf{u}(t)$ in Eq. (7.18), the control error reads:

$$\dot{\mathbf{e}}(t) = -\boldsymbol{\Gamma}\,\mathbf{e}(t) + \mathbf{F}\Big(\hat{\mathbf{r}}_u(t) - \mathbf{r}_u\big(\mathbf{x}(t)\big)\Big), \qquad \mathbf{e}(0) = \mathbf{x}^s(0) - \mathbf{x}(0). \tag{7.22}$$

The estimation bias will be small if the unknown rates are continuous and do not vary much over the time window $[t - \Delta t, t]$, as shown in Appendix D.3. Reducing the size q of the filter window is likely to reduce the bias (since Δt decreases) but will result in a larger variance, as shown by Eq. (5.29).

As indicated by Eq. (7.22), the impact of the estimation bias on the control error can be

reduced by the use of large gains $\mathbf{\Gamma}$ until the fast states reach steady state. Once these states are nearly constant, the unknown rates become constant as well, and their estimated values approach the true values. This allows reducing the gains $\mathbf{\Gamma}$, thereby obtaining smoother input and state profiles for accurate estimation of the plant steady state.

7.4.1.3 Example: Control of a CSTR

In the CSTR example, besides the structure already given in Eq. (7.8), it is also possible to define

$$\mathbf{B}_a\big(\mathbf{x}(t)\big) := \begin{bmatrix}\mathbf{b} & \mathscr{C}\end{bmatrix} - \begin{bmatrix}Q(t)\\ \mathbf{n}_R(t)\end{bmatrix}\begin{bmatrix}0 & \mathbf{k}_{in}^{\mathrm{T}}\end{bmatrix}, \qquad \boldsymbol{\beta}_a\big(\mathbf{x}(t)\big) := \mathbf{0}_{S_R+1}. \tag{7.23}$$

Hence, one computes the physical inputs $\mathbf{u}(t)$ according to Eqs. (7.19)–(7.20):

$$\begin{bmatrix}q_{ex}(t)\\ \mathbf{u}_{in}(t)\end{bmatrix} = \mathbf{B}_a\big(\tilde{\mathbf{x}}(t)\big)^{-1}\left(\begin{bmatrix}\dot{Q}^s(t)\\ \dot{\mathbf{n}}_R^s(t)\end{bmatrix} + \mathbf{\Gamma}\left(\begin{bmatrix}Q^s(t)\\ \mathbf{n}_R^s(t)\end{bmatrix} - \begin{bmatrix}\tilde{Q}(t)\\ \tilde{\mathbf{n}}_R(t)\end{bmatrix}\right) - \begin{bmatrix}-\mathbf{\Delta H}_r^{\mathrm{T}}\\ \mathbf{N}_R^{\mathrm{T}}\end{bmatrix}\hat{\mathbf{r}}_v(t)\right). \tag{7.24}$$

Note that $\mathbf{B}_a\big(\mathbf{x}(t)\big)$ is invertible if and only if $S_I = S_R - S_F \leq 1$, that is, if there is at most one non-fed species that affects the reaction rates, a very likely situation. Hence, the fast states of a CSTR can typically be controlled quite efficiently. Note also that the control law in Eq. (7.24) does not rely on kinetic models since the values of the reaction rates $\mathbf{r}_v(t)$ are estimated from measurements of flowrates, reactor temperature, reactor volume and some of the concentrations. However, the procedure requires the knowledge of stoichiometry, inlet concentrations and reaction enthalpies.

7.4.2 Estimation of plant steady state during transient operation

This section shows how one can estimate the steady state of the slow states $\mathbf{z}$ during transient operation.

7.4.2.1 Rate-based estimation of $\bar{\mathbf{z}}_k$

Using the static version of Eq. (7.4), the steady-state values $\bar{\mathbf{z}}_k$ of the slow states are estimated from $\bar{\mathbf{x}}_k$ and $\bar{\mathbf{u}}_k$ from the static relationship:

$$\mathbf{H}\,\hat{\bar{\mathbf{r}}}_{u,k} + \mathbf{h}_a(\bar{\mathbf{x}}_k, \hat{\bar{\mathbf{z}}}_k, \bar{\mathbf{u}}_k) = \mathbf{0}_{n_z}. \tag{7.25}$$

Since $\frac{\partial \mathbf{h}_a}{\partial \mathbf{z}}\big(\mathbf{x},\mathbf{z},\mathbf{u}\big)$ is invertible according to Assumption 7.3, the implicit function theorem implies that the solution $\hat{\bar{\mathbf{z}}}_k$ to Eq. (7.25) is unique.

In particular, if $\mathbf{h}_a\big(\mathbf{x}(t),\mathbf{z}(t),\mathbf{u}(t)\big)$ can be expressed as linear combinations of $\mathbf{z}(t)$ as:

$$\mathbf{h}_a\big(\mathbf{x}(t),\mathbf{z}(t),\mathbf{u}(t)\big) := \mathbf{H}_a\big(\mathbf{x}(t),\mathbf{u}(t)\big)\,\mathbf{z}(t), \tag{7.26}$$

with $\mathbf{H}_a\big(\mathbf{x}(t),\mathbf{u}(t)\big)$ being an $(n_z \times n_z)$-dimensional matrix, then the steady-state values $\bar{\mathbf{z}}_k$ are estimated explicitly as

$$\hat{\bar{\mathbf{z}}}_k = -\mathbf{H}_a(\bar{\mathbf{x}}_k,\bar{\mathbf{u}}_k)^{-1}\,\mathbf{H}\,\hat{\bar{\mathbf{r}}}_{u,k}, \tag{7.27}$$

since $\mathbf{H}_a(\mathbf{x},\mathbf{u}) = \frac{\partial \mathbf{h}_a}{\partial \mathbf{z}}\big(\mathbf{x},\mathbf{z},\mathbf{u}\big)$ is invertible.

The slow states $\hat{\bar{\mathbf{z}}}_k$ are computed as an n_z-dimensional function $\mathbf{s}(\bar{\mathbf{x}}_k,\bar{\mathbf{u}}_k,\hat{\bar{\mathbf{r}}}_{u,k})$, either implicitly from Eq. (7.25) or explicitly from Eq. (7.27). This estimation can be performed *before* the slow states $\mathbf{z}(t)$ converge to their steady-state values $\bar{\mathbf{z}}_k$. This implies that one only needs to wait for the steady state of the fast states $\mathbf{x}$ to estimate the steady state of the slow states $\mathbf{z}$. This steady state of $\mathbf{z}$ is a stable equilibrium point and can be reached without feedback control of $\mathbf{z}$ since $\mathbf{z}$ is open-loop stable according to Assumption 7.3.

Remark 7.1. The assumption that $\mathbf{h}_u(\mathbf{x},\mathbf{u})$ in Eq. (7.4) does not depend on the slow states $\mathbf{z}$ is needed because the steady-state rates $\mathbf{H}\,\hat{\bar{\mathbf{r}}}_{u,k}$ need to be reached as soon as the fast states $\mathbf{x}$ reach steady state. Without this assumption, it would be necessary to wait for the steady state of $\mathbf{z}$ to obtain the steady-state rates $\mathbf{H}\,\hat{\bar{\mathbf{r}}}_{u,k}$.

The following proposition quantifies the quality of the estimates $\hat{\bar{\mathbf{z}}}_k$ in terms of their variance.

Proposition 7.2. *Let $\hat{\bar{\mathbf{r}}}_{u,k}$ be estimated as shown in Section 7.3.2, the inputs $\bar{\mathbf{u}}_k$ be computed according to the control laws presented in Section 7.4.1.2, and the estimates $\hat{\bar{\mathbf{z}}}_k$ be given by the function*

$$\hat{\bar{\mathbf{z}}}_k = \mathbf{s}(\bar{\mathbf{x}}_k,\bar{\mathbf{u}}_k,\hat{\bar{\mathbf{r}}}_{u,k}). \tag{7.28}$$

Then, the variance of $\hat{\bar{\mathbf{z}}}_k$ is

$$\begin{aligned}\mathrm{Var}\left[\hat{\bar{\mathbf{z}}}_k\right] = {}& \frac{\partial \mathbf{s}}{\partial \bar{\mathbf{u}}_k}(\bar{\mathbf{x}}_k,\bar{\mathbf{u}}_k,\hat{\bar{\mathbf{r}}}_{u,k})\,\mathbf{B}_a\big(\bar{\mathbf{x}}_k\big)^{-1}\,\mathbf{F}\,\mathrm{Var}\left[\hat{\bar{\mathbf{r}}}_{u,k}\right]\,\mathbf{F}^{\mathrm{T}}\left(\mathbf{B}_a\big(\bar{\mathbf{x}}_k\big)^{-1}\right)^{\mathrm{T}}\frac{\partial \mathbf{s}}{\partial \bar{\mathbf{u}}_k}(\bar{\mathbf{x}}_k,\bar{\mathbf{u}}_k,\hat{\bar{\mathbf{r}}}_{u,k})^{\mathrm{T}} \\ & + \frac{\partial \mathbf{s}}{\partial \hat{\bar{\mathbf{r}}}_{u,k}}(\bar{\mathbf{x}}_k,\bar{\mathbf{u}}_k,\hat{\bar{\mathbf{r}}}_{u,k})\,\mathrm{Var}\left[\hat{\bar{\mathbf{r}}}_{u,k}\right]\,\frac{\partial \mathbf{s}}{\partial \hat{\bar{\mathbf{r}}}_{u,k}}(\bar{\mathbf{x}}_k,\bar{\mathbf{u}}_k,\hat{\bar{\mathbf{r}}}_{u,k})^{\mathrm{T}}.\end{aligned} \tag{7.29}$$

In particular, if $\hat{\bar{\mathbf{z}}}_k$ is computed from Eq. (7.27)*, then*

$$\frac{\partial \mathbf{s}}{\partial \bar{u}_{j,k}}(\bar{\mathbf{x}}_k,\bar{\mathbf{u}}_k,\hat{\bar{\mathbf{r}}}_{u,k}) = -\mathbf{H}_a(\bar{\mathbf{x}}_k,\bar{\mathbf{u}}_k)^{-1}\,\frac{\partial \mathbf{H}_a}{\partial \bar{u}_{j,k}}(\bar{\mathbf{x}}_k,\bar{\mathbf{u}}_k)\,\hat{\bar{\mathbf{z}}}_k, \qquad \forall j = 1,\ldots,n_u, \tag{7.30}$$

$$\frac{\partial \mathbf{s}}{\partial \hat{\bar{\mathbf{r}}}_{u,k}}(\bar{\mathbf{x}}_k,\bar{\mathbf{u}}_k,\hat{\bar{\mathbf{r}}}_{u,k}) = -\mathbf{H}_a(\bar{\mathbf{x}}_k,\bar{\mathbf{u}}_k)^{-1}\,\mathbf{H}. \tag{7.31}$$

Proof. The proof is given in Appendix F.1. □

7.4.2.2 Example: Estimation of plant steady state during transient operation of a CSTR

The reaction rates and steady-state values in a CSTR are easily estimated using the concept of extents presented in Section 2.5. The approach is detailed next for the case of steady-state estimation.

Let us recall an important result from the concept of extents. The states $Q(t)$, $\mathbf{n}_R(t)$ and $\mathbf{n}_P(t)$ can be expressed as combinations of the various extents, as shown in Section 2.5:

$$\begin{bmatrix} Q(t) \\ \mathbf{n}_R(t) \end{bmatrix} = \begin{bmatrix} -\boldsymbol{\Delta}\mathbf{H}_r^{\mathrm{T}} \\ \mathbf{N}_R^{\mathrm{T}} \end{bmatrix} \mathbf{x}_r(t) + \begin{bmatrix} \mathbf{b} & \mathscr{C} \end{bmatrix} \begin{bmatrix} x_{ex}(t) \\ \mathbf{x}_{in}(t) \end{bmatrix} + \begin{bmatrix} Q_0 \\ \mathbf{n}_{R,0} \end{bmatrix} x_{ic}(t), \tag{7.32}$$

$$\mathbf{n}_P(t) = \mathbf{N}_P^{\mathrm{T}} \mathbf{x}_r(t) + \mathbf{n}_{P,0} x_{ic}(t), \tag{7.33}$$

where $\mathbf{x}_r$ are the R extents of reaction, x_{ex} the extent of heat exchange, $\mathbf{x}_{in}$ the p extents of inlet, and x_{ic} the extent of initial conditions. These extents are described in their differential form as:

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t), \qquad \mathbf{x}_r(0) = \mathbf{0}_R, \tag{7.34}$$

$$\dot{x}_{ex}(t) = q_{ex}(t) - \omega(t)x_{ex}(t), \qquad x_{ex}(0) = 0, \tag{7.35}$$

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) - \omega(t)\mathbf{x}_{in}(t), \qquad \mathbf{x}_{in}(0) = \mathbf{0}_p, \tag{7.36}$$

$$\dot{x}_{ic}(t) = -\omega(t)x_{ic}(t), \qquad x_{ic}(0) = 1. \tag{7.37}$$

Let us assume that the heat Q and the numbers of moles $\mathbf{n}_R$ are controlled by manipulating q_{ex} and $\mathbf{u}_{in}$. Then, as soon as feedback control enforces convergence of $Q(t)$ and $\mathbf{n}_R(t)$ to the steady-state setpoints $\bar{Q}^s$ and $\bar{\mathbf{n}}_R^s$, the manipulated variables also converge to $\bar{q}_{ex}$ and $\bar{\mathbf{u}}_{in}$. It follows that, at steady state, one can compute the extent of heat exchange as $\bar{x}_{ex} = \frac{\bar{q}_{ex}}{\bar{\omega}}$, the extents of inlet as $\bar{\mathbf{x}}_{in} = \frac{\bar{\mathbf{u}}_{in}}{\bar{\omega}}$, and the extent of initial conditions as $\bar{x}_{ic} = 0$. As a result, the extents of reaction at steady state, $\bar{\mathbf{x}}_r = \frac{\bar{\mathbf{r}}_v}{\bar{\omega}}$, can be estimated *without kinetic models* as

$$\hat{\bar{\mathbf{x}}}_r = \mathscr{T}\left(\begin{bmatrix} \bar{Q} \\ \bar{\mathbf{n}}_R \end{bmatrix} - \begin{bmatrix} \mathbf{b} & \mathscr{C} \end{bmatrix} \begin{bmatrix} \bar{x}_{ex} \\ \bar{\mathbf{x}}_{in} \end{bmatrix} \right), \tag{7.38}$$

where $\mathscr{T}$ is such that $\mathscr{T} \begin{bmatrix} -\boldsymbol{\Delta}\mathbf{H}_r^{\mathrm{T}} \\ \mathbf{N}_R^{\mathrm{T}} \end{bmatrix} = \mathbf{I}_R$.

Finally, the steady-state values $\hat{\bar{\mathbf{n}}}_P$ can be computed as:

$$\hat{\bar{\mathbf{n}}}_P = \mathbf{N}_P^{\mathrm{T}} \hat{\bar{\mathbf{x}}}_r, \tag{7.39}$$

which can be done *before* $\mathbf{n}_P(t)$ reaches steady state.

Remark 7.2. The CSTR model in Eq. (7.8) has the linear structure of Eq. (7.26). As a result, $\mathbf{H}_a\big(\mathbf{u}(t)\big) := -\omega(t)\mathbf{I}_{S_p}$ is a diagonal matrix with all diagonal elements equal to $-\omega(t)$, which allows simplifying Eq. (7.27) and leads to the same result, as follows:

$$\hat{\bar{\mathbf{n}}}_P = \hat{\bar{\mathbf{z}}} = -\mathbf{H}_a^{-1}(\bar{\mathbf{u}})\,\mathbf{H}\,\hat{\bar{\mathbf{r}}}_u = \mathbf{N}_P^{\mathrm{T}}\,\frac{\hat{\bar{\mathbf{r}}}_v}{\bar{\omega}} = \mathbf{N}_P^{\mathrm{T}}\,\hat{\bar{\mathbf{x}}}_r. \tag{7.40}$$

Remark 7.3. If the temperature and the concentrations of all the species that affect the reaction rates are controlled, then, when $Q(t)$ and $\mathbf{n}_R(t)$ reach steady state, the reaction rates also reach the steady-state values $\bar{\mathbf{r}}_v$. From that point on, the numbers of moles $\mathbf{n}_P$ follow the dynamics

$$\dot{\mathbf{n}}_P(t) = \mathbf{N}_P^{\mathrm{T}}\,\bar{\mathbf{r}}_v - \bar{\omega}\,\mathbf{n}_P(t). \tag{7.41}$$

This implies that the residence time $\bar{\omega}^{-1}$ becomes the dominant time constant associated with the states $\mathbf{n}_P$. Since the steady states $\bar{\mathbf{n}}_P$ do not have to be reached to estimate $\hat{\bar{\mathbf{r}}}_u$ and $\hat{\bar{\mathbf{z}}}$, the time constant $\bar{\omega}^{-1}$ is a measure of the time saved thanks to rate estimation. This time constant can be compared to α^{-1} and Δt, which express the time needed to reach $\bar{\mathbf{x}}$ and estimate $\hat{\bar{\mathbf{r}}}_u$ and $\hat{\bar{\mathbf{z}}}$.

In summary, in this work, instead of waiting for the steady state of the (slow) product concentrations, one can take advantage of (i) feedback control to speed up the convergence of the (fast) reactant concentrations, and (ii) measurement-based rate estimation to estimate the steady-state product concentrations as soon as the fast states reach steady state.

7.4.3 Example: Fast estimation of plant steady state in a CSTR

This section illustrates the fast estimation of plant steady state for a homogeneous CSTR of constant volume and constant density. The purpose is to illustrate how the choice of CVs and MVs and the use of feedback control and rate estimation can improve the speed at which the plant steady state can be estimated.

7.4.3.1 Plant description

We consider a CSTR with the two reactions A + B → C and 2B → D. The same reaction system has already been investigated with regard to both control (in Section 6.3) and optimization [137]. We briefly present the balance equations, using the same notation as in Section 2.2. The states are the heat Q and the numbers of moles n_{A}, n_{B}, n_{C} and n_{D}. Assuming that the volume and the density of the reaction mixture remain constant and the inlet streams are at reference conditions and do not contribute to the heat balance, the dynamic

equations read:

$$\dot{Q}(t) = -\boldsymbol{\Delta}\mathbf{H}_r^{\mathrm{T}}\mathbf{r}_v(t) + q_{ex}(t) - \frac{F_{\mathrm{A}}(t)+F_{\mathrm{B}}(t)}{V}Q(t), \qquad Q(0) = Q_0, \tag{7.42a}$$

$$\dot{n}_{\mathrm{A}}(t) = \mathbf{N}_{\mathrm{A}}^{\mathrm{T}}\mathbf{r}_v(t) + c_{in,\mathrm{A}}F_{\mathrm{A}}(t) - \frac{F_{\mathrm{A}}(t)+F_{\mathrm{B}}(t)}{V}n_{\mathrm{A}}(t), \qquad n_{\mathrm{A}}(0) = n_{\mathrm{A},0}, \tag{7.42b}$$

$$\dot{n}_{\mathrm{B}}(t) = \mathbf{N}_{\mathrm{B}}^{\mathrm{T}}\mathbf{r}_v(t) + c_{in,\mathrm{B}}F_{\mathrm{B}}(t) - \frac{F_{\mathrm{A}}(t)+F_{\mathrm{B}}(t)}{V}n_{\mathrm{B}}(t), \qquad n_{\mathrm{B}}(0) = n_{\mathrm{B},0}, \tag{7.42c}$$

$$\dot{n}_{\mathrm{C}}(t) = \mathbf{N}_{\mathrm{C}}^{\mathrm{T}}\mathbf{r}_v(t) - \frac{F_{\mathrm{A}}(t)+F_{\mathrm{B}}(t)}{V}n_{\mathrm{C}}(t), \qquad n_{\mathrm{C}}(0) = n_{\mathrm{C},0}, \tag{7.42d}$$

$$\dot{n}_{\mathrm{D}}(t) = \mathbf{N}_{\mathrm{D}}^{\mathrm{T}}\mathbf{r}_v(t) - \frac{F_{\mathrm{A}}(t)+F_{\mathrm{B}}(t)}{V}n_{\mathrm{D}}(t), \qquad n_{\mathrm{D}}(0) = n_{\mathrm{D},0}, \tag{7.42e}$$

with

$$\mathbf{r}_v(t) := V\,\boldsymbol{\varphi}\big(Q(t), n_{\mathrm{A}}(t), n_{\mathrm{B}}(t)\big). \tag{7.43}$$

In this model, F_{A} is the volumetric flowrate of the inlet stream for species A with concentration $c_{in,\mathrm{A}}$, and F_{B} is the volumetric flowrate of the inlet stream for species B with concentration $c_{in,\mathrm{B}}$. The outlet flowrate is assumed to be equal to the sum of the inlet flowrates. The inputs are $q_{ex}(t)$, $F_{\mathrm{A}}(t)$ and $F_{\mathrm{B}}(t)$.

The corresponding steady-state model reads:

$$0 = -\boldsymbol{\Delta}\mathbf{H}_r^{\mathrm{T}}\bar{\mathbf{r}}_v + \bar{q}_{ex} - \frac{\bar{F}_{\mathrm{A}}+\bar{F}_{\mathrm{B}}}{V}\bar{Q}, \tag{7.44a}$$

$$0 = \mathbf{N}_{\mathrm{A}}^{\mathrm{T}}\bar{\mathbf{r}}_v + c_{in,\mathrm{A}}\bar{F}_{\mathrm{A}} - \frac{\bar{F}_{\mathrm{A}}+\bar{F}_{\mathrm{B}}}{V}\bar{n}_{\mathrm{A}}, \tag{7.44b}$$

$$0 = \mathbf{N}_{\mathrm{B}}^{\mathrm{T}}\bar{\mathbf{r}}_v + c_{in,\mathrm{B}}\bar{F}_{\mathrm{B}} - \frac{\bar{F}_{\mathrm{A}}+\bar{F}_{\mathrm{B}}}{V}\bar{n}_{\mathrm{B}}, \tag{7.44c}$$

$$0 = \mathbf{N}_{\mathrm{C}}^{\mathrm{T}}\bar{\mathbf{r}}_v - \frac{\bar{F}_{\mathrm{A}}+\bar{F}_{\mathrm{B}}}{V}\bar{n}_{\mathrm{C}}, \tag{7.44d}$$

$$0 = \mathbf{N}_{\mathrm{D}}^{\mathrm{T}}\bar{\mathbf{r}}_v - \frac{\bar{F}_{\mathrm{A}}+\bar{F}_{\mathrm{B}}}{V}\bar{n}_{\mathrm{D}}, \tag{7.44e}$$

with

$$\bar{\mathbf{r}}_v := V\,\boldsymbol{\varphi}(\bar{Q}, \bar{n}_{\mathrm{A}}, \bar{n}_{\mathrm{B}}). \tag{7.45}$$

In this dynamic model, the fast states are $Q(t)$, $n_{\mathrm{A}}(t)$ and $n_{\mathrm{B}}(t)$, while the slow states are $n_{\mathrm{C}}(t)$ and $n_{\mathrm{D}}(t)$. Note that the fast states affect the slow states, but the slow states do not affect the fast states. Hence, the states and inputs of the generic Model (7.3)–(7.4) are:

$$\mathbf{u}(t) := \begin{bmatrix} q_{ex}(t) \\ F_{\mathrm{A}}(t) \\ F_{\mathrm{B}}(t) \end{bmatrix}, \qquad \mathbf{x}(t) := \begin{bmatrix} Q(t) \\ n_{\mathrm{A}}(t) \\ n_{\mathrm{B}}(t) \end{bmatrix}, \qquad \mathbf{z}(t) := \begin{bmatrix} n_{\mathrm{C}}(t) \\ n_{\mathrm{D}}(t) \end{bmatrix}, \tag{7.46}$$

which results in the following definitions:

$$\mathbf{r}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big) := \mathbf{r}_v(t), \qquad \mathbf{s}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big) := \mathbf{0}_{S_R+1}, \tag{7.47}$$

$$\mathbf{f}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big) := \begin{bmatrix} -\boldsymbol{\Delta}\mathbf{H}_r^{\mathrm{T}} \\ \mathbf{N}_{\mathrm{A}}^{\mathrm{T}} \\ \mathbf{N}_{\mathrm{B}}^{\mathrm{T}} \end{bmatrix} \mathbf{r}_v(t), \qquad \mathbf{F} := \begin{bmatrix} -\boldsymbol{\Delta}\mathbf{H}_r^{\mathrm{T}} \\ \mathbf{N}_{\mathrm{A}}^{\mathrm{T}} \\ \mathbf{N}_{\mathrm{B}}^{\mathrm{T}} \end{bmatrix}, \tag{7.48}$$

$$\mathbf{f}_a\big(\mathbf{x}(t),\mathbf{u}(t)\big) := \begin{bmatrix} 1 & 0 & 0 \\ 0 & c_{in,\mathrm{A}} & 0 \\ 0 & 0 & c_{in,\mathrm{B}} \end{bmatrix} \begin{bmatrix} q_{ex}(t) \\ F_{\mathrm{A}}(t) \\ F_{\mathrm{B}}(t) \end{bmatrix} - \frac{F_{\mathrm{A}}(t)+F_{\mathrm{B}}(t)}{V} \begin{bmatrix} Q(t) \\ n_{\mathrm{A}}(t) \\ n_{\mathrm{B}}(t) \end{bmatrix}, \tag{7.49}$$

$$\mathbf{h}_u\big(\mathbf{x}(t),\mathbf{u}(t)\big) := \begin{bmatrix} \mathbf{N}_{\mathrm{C}}^{\mathrm{T}} \\ \mathbf{N}_{\mathrm{D}}^{\mathrm{T}} \end{bmatrix} \mathbf{r}_v(t), \qquad \mathbf{H} := \begin{bmatrix} \mathbf{N}_{\mathrm{C}}^{\mathrm{T}} \\ \mathbf{N}_{\mathrm{D}}^{\mathrm{T}} \end{bmatrix}, \tag{7.50}$$

$$\mathbf{h}_a\big(\mathbf{z}(t),\mathbf{u}(t)\big) := -\frac{F_{\mathrm{A}}(t)+F_{\mathrm{B}}(t)}{V} \begin{bmatrix} n_{\mathrm{C}}(t) \\ n_{\mathrm{D}}(t) \end{bmatrix}. \tag{7.51}$$

Regarding the control aspect, it is possible to use feedback linearization to drive the fast states $Q(t)$, $n_{\mathrm{A}}(t)$ and $n_{\mathrm{B}}(t)$ to the setpoints $\bar{Q}^s$, $\bar{n}_{\mathrm{A}}^s$ and $\bar{n}_{\mathrm{B}}^s$ by manipulating the inputs $q_{ex}(t)$, $F_{\mathrm{A}}(t)$ and $F_{\mathrm{B}}(t)$. Control via rate estimation and feedback linearization is used here since it is known from previous work that this control scheme is quite efficient to control the temperature and the concentrations of species that are fed to the reactor, as shown in Section 6.3. The choice of the fast states Q, n_{A} and n_{B} as CVs is straightforward.

7.4.3.2 Simulation model and measurements

The parameter values used in the simulation are taken from [137], except for the rate constants that have been modified and the heat exchange rates and flowrates that have have been increased approximately 200 times. The model parameters and operating conditions are given in Table 7.1. The CSTR is simulated using the following rate laws:

$$q_{ex}(t) = UA(T_j(t) - T(t)), \tag{7.52}$$

$$r_{v,1}(t) = Vk_{1,ref} \exp\left(\frac{E_{a,1}}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T(t)}\right)\right) \frac{n_{\mathrm{A}}(t)}{V}\frac{n_{\mathrm{B}}(t)}{V}, \tag{7.53}$$

$$r_{v,2}(t) = Vk_{2,ref} \exp\left(\frac{E_{a,2}}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T(t)}\right)\right) \left(\frac{n_{\mathrm{B}}(t)}{V}\right)^2, \tag{7.54}$$

which of course are assumed to be unknown for the purpose of rate estimation.

The concentration measurements are corrupted with additive zero-mean Gaussian noise with a standard deviation of 1% of the corresponding maximal concentration, while the temperature measurements are corrupted with additive zero-mean Gaussian noise with a standard deviation of 0.08 K. The concentrations of A and B are assumed to be measured every 1.5 s for the purpose of feedback control.

Table 7.1 – Model parameters and operating conditions.

Variable	Value	Units
$k_{1,ref}$	1.06	l mol^{-1} min^{-1}
$k_{2,ref}$	2.56	l mol^{-1} min^{-1}
$E_{a,1}$	20	kJ mol^{-1}
$E_{a,2}$	10	kJ mol^{-1}
R	8.314	kJ kmol^{-1} K^{-1}
T_{ref}	298.15	K
UA	100	kJ min^{-1} K^{-1}
$(-\Delta H_{r,1})$	70	kJ mol^{-1}
$(-\Delta H_{r,2})$	100	kJ mol^{-1}
$c_{in,\mathrm{A}}$	2.0	mol l^{-1}
$c_{in,\mathrm{B}}$	1.5	mol l^{-1}
V	500	l
$V\rho c_p$	736.3	kJ K^{-1}

7.4.3.3 Fast estimation of plant steady state

The procedure requires the tuning of two main parameters, namely, the window size Δt of the differentiation filter used for rate estimation and the controller gains $\mathbf{\Gamma}$ used for feedback control. With respect to controller tuning, we propose to use large controller gains until the fast states reach steady state and then smaller gains to reduce the signal variability. Two rate estimates with different window sizes of the differentiation filter will be considered.

Figure 7.1 presents these simulation results. The top row shows the evolution of the CVs, which are the fast states $Q(t)$, $n_{\mathrm{A}}(t)$ and $n_{\mathrm{B}}(t)$, while the second row shows the time profile of the MVs, which are the inputs $q_{ex}(t)$, $F_{\mathrm{A}}(t)$ and $F_{\mathrm{B}}(t)$. The setpoint of $Q(t)$ remains unchanged, while the setpoint of $n_{\mathrm{A}}(t)$ is increased and the setpoint of $n_{\mathrm{B}}(t)$ is decreased. The first two columns of the last two rows represent the rate estimates $\hat{r}_{v,1}(t)$ and $\hat{r}_{v,2}(t)$ for window sizes of the differentiation filter of $\Delta t = 3$ min (first column) and $\Delta t = 10$ min (second column), as well as the values of the simulated reaction rates $r_{v,1}(t)$ and $r_{v,2}(t)$. Note that the rate estimates obtained with the smallest window size are used to manipulate $q_{ex}(t)$, $F_{\mathrm{A}}(t)$ and $F_{\mathrm{B}}(t)$ via feedback control, whereas the estimates that result from the largest window size are used to estimate the steady-state values of the reaction rates $\bar{r}_{v,1}$ and $\bar{r}_{v,2}$, the inputs $\bar{q}_{ex}$, $\bar{F}_{\mathrm{A}}$ and $\bar{F}_{\mathrm{B}}$ and the slow states $\bar{n}_{\mathrm{C}}$ and $\bar{n}_{\mathrm{D}}$. The last column of the last two rows represents the time profiles of the slow states $n_{\mathrm{C}}(t)$ and $n_{\mathrm{D}}(t)$ and the corresponding steady-state estimates at each instant.

The controller gains for the control of $n_{\mathrm{A}}(t)$ and $n_{\mathrm{B}}(t)$ are reduced by a factor of 5 when the fast states reach steady state, which occurs after 6 min. The initial controller gains cause a large variability of the inputs, which results in a large variability of the reaction

rates. Hence, the controller should not be more aggressive at this stage, not because of stability issues, but because the induced variability impacts the precision of the estimated rates. However, these large controller gains are useful since they result in fast convergence of the CVs to their setpoints. The reaction rate estimates obtained with the smallest window size exhibit a larger variability than the estimates that result from the largest window size. Nevertheless, the former estimates are more suited for feedback control since they provide faster estimation of the reaction rates, while the latter estimates are more suited for steady-state estimation owing to their smaller variance. The combination of large controller gains that enforce the convergence of the fast states to steady state after 6 min with the rate estimator that uses a window size of 10 min for steady-state estimation allows accurate estimation of the steady-state reaction rates, inputs and slow states after approximately 16 min. Note that, at that time, $n_C(t)$ and $n_D(t)$ are still moving, which shows that the plant steady state can be estimated before it is actually reached.

One advantage of the method used for measurement-based rate estimation in this study is that the variance of the rate estimates can be computed analytically from the variance of the individual measurements according to Eq. (5.29). Figure 7.2 shows the standard deviations of the two rate estimates for different window sizes Δt of the differentiation filter, including the sizes of 3 min and 10 min that are used in this study.

7.5 Static Real-time Optimization

This section discusses the application to static real-time optimization of the approach for fast estimation of plant steady state presented in the previous sections.

7.5.1 Four RTO configurations

Measurement-based rate estimation and feedback control can be used to speed up the estimation of plant steady state in four distinct RTO configurations: (i) without feedback control and without rate estimation (Figure 7.3), which is the classical configuration (for example, see [138], where the classical formulation of the Williams-Otto reactor problem is given, with some of the decision variables being physical inputs rather than setpoints for controlled states or outputs of the reactor), (ii) with feedback control but without rate estimation (Figure 7.4), (iii) without feedback control but with rate estimation (Figure 7.5), and (iv) with feedback control and with rate estimation (Figure 7.6). The main features are as follows (described here for the kth iteration):

1. Feedback control (Figures 7.4 and 7.6) helps drive $\mathbf{x}(t)$ quickly to the steady-state setpoints $\bar{\mathbf{x}}_k^s$ by manipulating the inputs $\mathbf{u}(t)$. Note that, if the number of states $\mathbf{x}$ is larger than the number of inputs $\mathbf{u}$, one typically specifies the setpoints $\bar{\mathbf{x}}_{c,k}^s$ of a subset or a linear combination of the fast states, the cardinality of which corresponds to the number of inputs. The setpoints $\bar{\mathbf{x}}_c^s$ should be such that (i) all the admissible values of the inputs $\bar{\mathbf{u}}$ can be reached by choosing some values of the setpoints $\bar{\mathbf{x}}_c^s$,

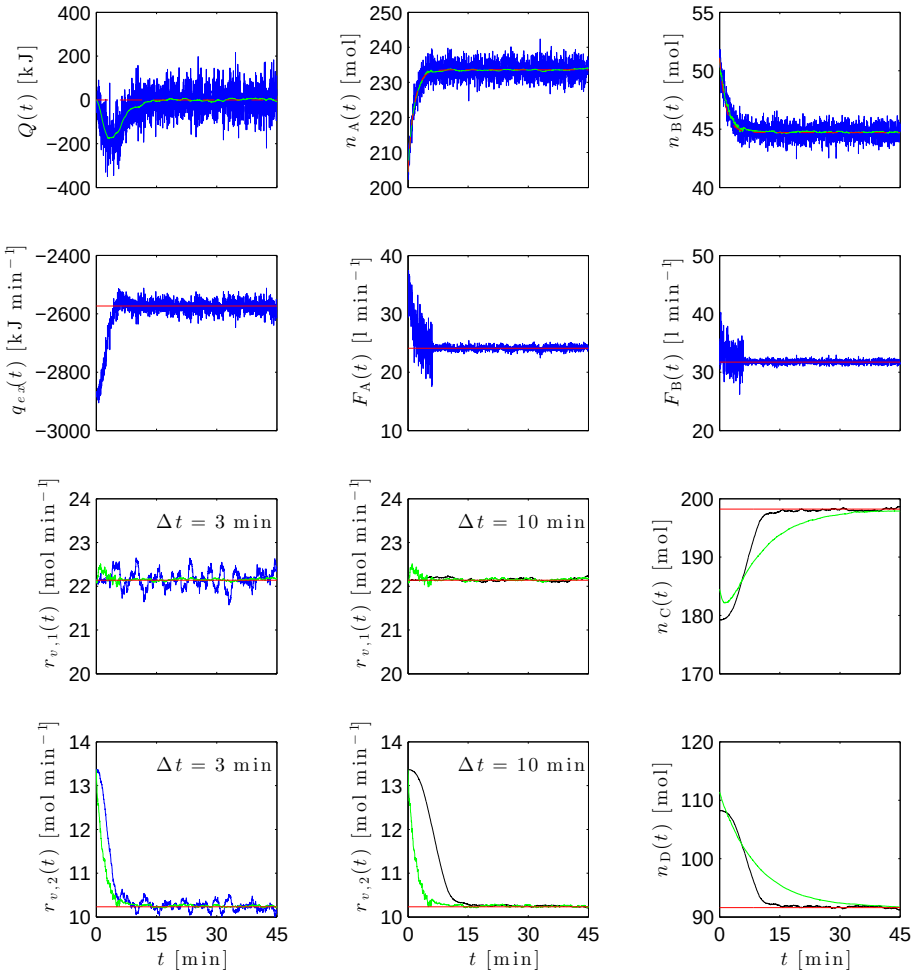

Figure 7.1 – Fast estimation of plant steady state, with large controller gains (first 6 min) followed by small controller gains. Time profiles of the CVs (top row), the MVs (second row), the reaction rates (last two rows, with $\Delta t = 3$ min in the first column and $\Delta t = 10$ min in the second column), and the slow states $n_C(t)$ and $n_D(t)$ (last column of the last two rows). Blue lines represent measured CVs, MVs computed via feedback control, and estimated reaction rates; black lines represent estimated steady-state values (for the reaction rates and the slow states); green lines represent true (simulated) values; dashed red lines represent setpoints; and solid red lines represent true steady-state values.

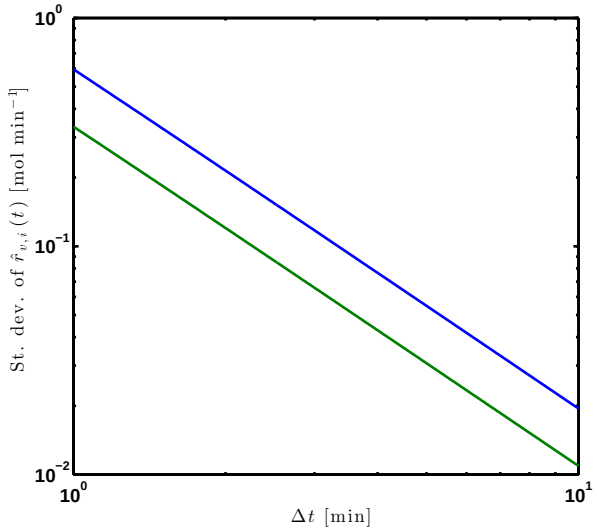

Figure 7.2 – Standard deviations of the rate estimates $\hat{r}_{v,1}$ (blue line) and $\hat{r}_{v,2}$ (green line) as functions of the window size Δt of the differentiation filter.

and (ii) the values of the setpoints $\bar{\mathbf{x}}_c^s$ lead to unique inputs $\bar{\mathbf{u}}$. In the discussion about RTO configurations that follows, it should be noted that (i) the RTO configurations without feedback control (i) and (iii) do not exclude the use of low-level controllers for relatively simple tasks such as the control of inlet flowrates or heat exchange power via manipulation of valve openings, and (ii) these configurations can also include cases where a feedback controller is used to stabilize the plant, and not to speed up the plant steady state. In contrast, in the RTO configurations with feedback control (ii) and (iv), the feedback controller is intentionally designed to speed up convergence of the fast states $\mathbf{x}(t)$ to steady state.

2. In the absence of rate estimation (Figures 7.3 and 7.4), one has to wait for both $\mathbf{x}(t)$ and $\mathbf{z}(t)$ to reach $\bar{\mathbf{x}}_k$ and $\bar{\mathbf{z}}_k$, whereas rate estimation (Figures 7.5 and 7.6) eliminates the need to wait for the slow states $\mathbf{z}(t)$ to reach the steady states $\bar{\mathbf{z}}_k$.
3. We propose to compute $\hat{\bar{\mathbf{z}}}_k$ from $\bar{\mathbf{x}}_k$ and $\bar{\mathbf{u}}_k$ in two steps: (i) as soon as $\mathbf{x}(t)$ and $\mathbf{u}(t)$ converge to $\bar{\mathbf{x}}_k$ and $\bar{\mathbf{u}}_k$, the rate-estimation block yields $\hat{\bar{\mathbf{r}}}_{u,k}$; (ii) then, the steady-state-estimation block computes $\hat{\bar{\mathbf{z}}}_k$ from $\hat{\bar{\mathbf{r}}}_{u,k}$ either implicitly using Eq. (7.25) or explicitly using Eq. (7.27).
4. At the end of the kth iteration, static RTO computes optimal values for the inputs $\bar{\mathbf{u}}_{k+1}$ (in the absence of feedback control) or for the setpoints $\bar{\mathbf{x}}_{c,k+1}^s$(in the presence of feedback control). The RTO problem reads (formulated here for the generic decision variables $\bar{\boldsymbol{\pi}}$ that represent either inputs or setpoints):

$$\bar{\boldsymbol{\pi}}_{k+1} = \arg\min_{\bar{\boldsymbol{\pi}}} \quad J_k(\bar{\boldsymbol{\pi}}) \tag{7.55a}$$

$$\text{s.t.} \quad \mathbf{g}_k(\bar{\boldsymbol{\pi}}) \leq \mathbf{0}, \tag{7.55b}$$

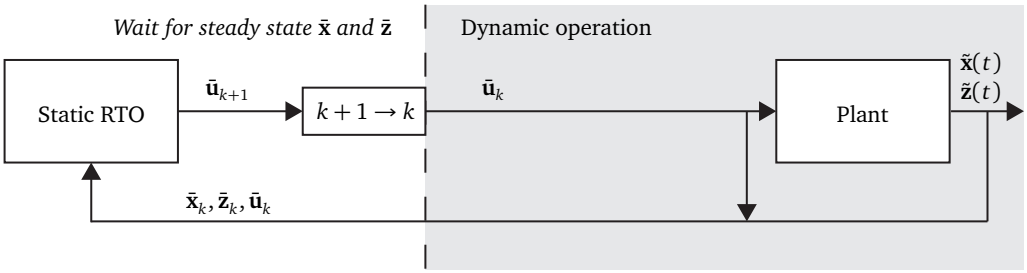

Figure 7.3 – Standard static RTO without feedback control and *without rate estimation*.

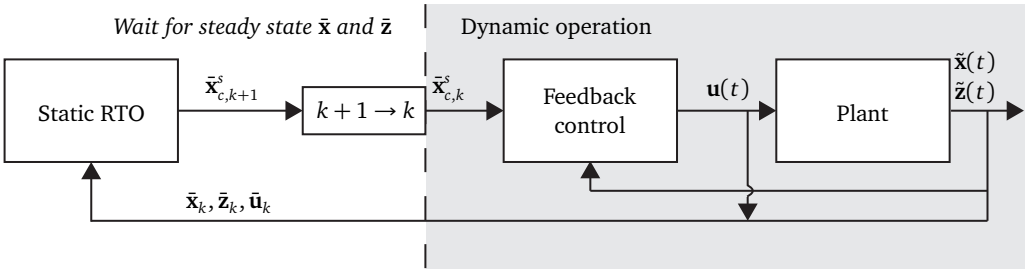

Figure 7.4 – Static RTO with feedback control but *without rate estimation*.

where J_k and $\mathbf{g}_k$ are the cost and constraints expressed as functions of the steady-state variables $\bar{\pi}$ at the end of the kth iteration.
To implement RTO, one typically optimizes the plant model via standard constrained optimization methods such as the sequential quadratic programming, interior point or active set algorithms [139]. However, in this study, a complete model is not available as only the rate functions $\mathbf{f}_a(\mathbf{x},\mathbf{u})$ and $\mathbf{h}_a(\mathbf{x},\mathbf{z},\mathbf{u})$ in Eqs. (7.3)–(7.4) are known, while the rates $\hat{\tilde{\mathbf{r}}}_{u,k}$ are estimated as time signals. Hence, one is forced to use an optimization algorithm that does not rely on a plant model, using for example evolutionary algorithms, NCO tracking with barrier-penalty function [137], or gradient-based optimization algorithms, whereby the gradients are estimated experimentally via finite-difference or similar methods, as proposed later in this chapter.

7.5.2 Comparison of RTO configurations

The static RTO schemes with rate estimation in Figures 7.5 and 7.6 are necessarily faster than the corresponding schemes without rate estimation in Figures 7.3 and 7.4, because one does not need to wait for the plant to reach steady state. In Figures 7.5 and 7.6, at each iteration, dynamic operation can be stopped as soon as the states $\mathbf{x}$ reach steady state, whereas in Figures 7.3 and 7.4 the dynamic operation ends when both $\mathbf{x}$ and $\mathbf{z}$ reach steady state. Note that, with rate estimation, it is not necessary to control $\mathbf{z}$, because the states $\mathbf{z}$ do not affect $\mathbf{x}$, and controlling $\mathbf{z}$ would not speed up reaching steady state for $\mathbf{x}$. Hence, even if both $\mathbf{x}$ and $\mathbf{z}$ were controlled in Figure 7.4, the time needed for $\mathbf{x}$ and $\mathbf{z}$ to reach

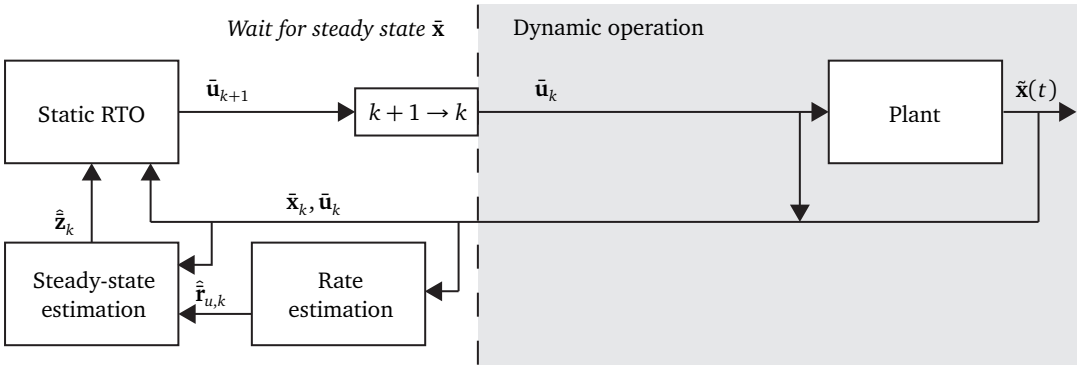

Figure 7.5 – Static RTO without feedback control but *with rate estimation*.

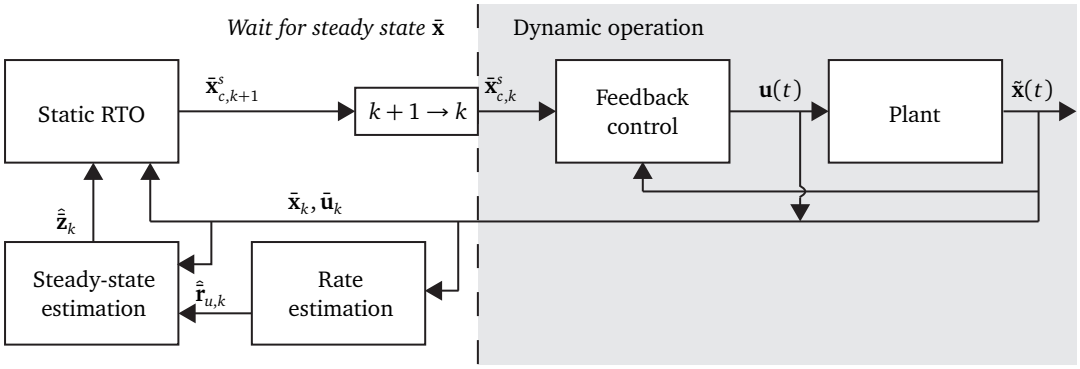

Figure 7.6 – Static RTO with feedback control and *with rate estimation*.

steady state would not be any shorter than the time needed for $\mathbf{x}$ to reach steady state when $\mathbf{x}$ is controlled. Moreover, to achieve similar closed-loop time responses, the controller gains necessary to control the fast states $\mathbf{x}$ are typically lower than those necessary to control both $\mathbf{x}$ and $\mathbf{z}$, thereby making the control scheme with only $\mathbf{x}$ less sensitive to measurement noise. Finally, the states $\mathbf{x}$ may be controllable in situations where the states $\mathbf{x}$ and $\mathbf{z}$ together are not controllable.

Comparing Figures 7.5 and 7.6, one can expect the steady state $\bar{\mathbf{x}}_k$ to be reached faster when $\mathbf{x}$ is controlled. The objective of the control scheme in Figure 7.6 is to drive the fast states $\mathbf{x}(t)$ to the constant setpoints $\bar{\mathbf{x}}_k^s$ in the shortest possible time after a step change in the setpoints $\bar{\mathbf{x}}_{c,k}^s$. This time is shorter than the time needed in Figure 7.5 after a step change in the inputs $\bar{\mathbf{u}}_k$. This shows that the scheme with rate estimation and feedback control in Figure 7.6 represents the fastest static RTO scheme, although at the price of requiring frequent measurements of $\mathbf{x}$ for feedback control.

7.5.3 Example: Static real-time optimization of a CSTR

This section shows the application of fast estimation of plant steady state to static RTO of the homogeneous CSTR of constant volume and constant density presented in Section 7.4.3.

7.5.3.1 Reformulation of the optimization problem

The use of control implies that the steady-state setpoints $\bar{n}_\mathrm{A}^s$ and $\bar{n}_\mathrm{B}^s$ can be seen as the decision variables for the RTO problem. Note that this differs from [137], where $\bar{F}_\mathrm{A}$ and $\bar{F}_\mathrm{B}$ were used as decision variables. However, both sets of decision variables determine a unique steady state, for which a cost function and a set of constraint functions can be written. Let us consider the optimization problem formulated in [137], but with $\bar{n}_\mathrm{A}^s$ and $\bar{n}_\mathrm{B}^s$ as decision variables:

$$\max_{\bar{n}_\mathrm{A}^s, \bar{n}_\mathrm{B}^s} \quad \phi = \frac{\left(\bar{F}_\mathrm{A} + \bar{F}_\mathrm{B}\right)^2 \left(\frac{\bar{n}_\mathrm{C}}{V}\right)^2}{\bar{F}_\mathrm{A} c_{in,\mathrm{A}}} \tag{7.56a}$$

$$\text{s.t.} \quad g_1 = \frac{\bar{F}_\mathrm{A} + \bar{F}_\mathrm{B}}{F_{out,max}} - 1 \leq 0 \tag{7.56b}$$

$$g_2 = \frac{\frac{\bar{F}_\mathrm{A} + \bar{F}_\mathrm{B}}{V} \bar{Q} - \bar{q}_{ex}}{q_{r,max}} - 1 \leq 0\,. \tag{7.56c}$$

The objective function ϕ of this maximization problem corresponds to the product of yield and productivity, whereas the constraints are related to the maximal outlet flowrate, $F_{out,max} = 76.7\,\mathrm{l\,min^{-1}}$, and the maximal heat power that can be generated by the reactions, $q_{r,max} = 3333\,\mathrm{kJ\,min^{-1}}$. Note that the cost function $-\phi$ still depends on the slow variable $\bar{n}_\mathrm{C}$. Here, the heat setpoint $\bar{Q}^s$ is kept constant for the sake of simplicity, but it could be considered as another decision variable as well.

As soon as $n_A(t)$ and $n_B(t)$ have converged toward their setpoints, $q_{ex}(t)$, $F_A(t)$, $F_B(t)$ and the reaction rates become constant. The rates $\bar{\mathbf{r}}_v$ can be evaluated via rate estimation. This, in turn, determines the values of the cost and constraints. In our example, Eq. (7.44d) allows expressing $\bar{n}_C$ as a function of $\bar{\mathbf{r}}_v$, which yields the estimate

$$\hat{\bar{n}}_C = \frac{V}{\bar{F}_A + \bar{F}_B} \mathbf{N}_C^T \hat{\bar{\mathbf{r}}}_v. \tag{7.57}$$

The number of moles $\bar{n}_C$ can be replaced by its estimate in the cost function of Problem (7.56), which can then be reformulated in terms of the fast quantities $\bar{F}_A$, $\bar{F}_B$ and $\hat{\bar{\mathbf{r}}}_v$:

$$\max_{\bar{n}_A^s, \bar{n}_B^s} \quad \phi = \frac{\left(\mathbf{N}_C^T \hat{\bar{\mathbf{r}}}_v\right)^2}{\bar{F}_A c_{in,A}} \tag{7.58a}$$

$$\text{s.t.} \quad g_1 = \frac{\bar{F}_A + \bar{F}_B}{F_{out,max}} - 1 \leq 0 \tag{7.58b}$$

$$g_2 = \frac{\frac{\bar{F}_A + \bar{F}_B}{V} \bar{Q} - \bar{q}_{ex}}{q_{r,max}} - 1 \leq 0. \tag{7.58c}$$

As soon as convergence to the setpoints $\bar{n}_A^s$ and $\bar{n}_B^s$ is enforced by the controller, $\bar{q}_{ex}$, $\bar{F}_A$, $\bar{F}_B$ and $\bar{\mathbf{r}}_v$ can be estimated and the values of the cost and constraints can be evaluated. Since it is expected that an efficient controller enforces fast convergence (less than 6 min in this particular example), the time needed to evaluate the cost and constraints can be reduced significantly, compared to the time that would be needed for the open-loop system to reach steady state (up to 48 min in this particular example).

An important issue is the effect of measurement noise in the computation of the cost and constraints, in particular if this computation depends on estimated quantities such as estimated reaction rates. This problem can be alleviated by using more data points for the estimation of the reaction rates, which implies that one has to wait a bit longer before the values of the cost and constraints can be obtained. In other words, a tradeoff between noise reduction and fast optimization needs to be considered in each application.

7.5.3.2 Implementation aspects

Two important implementation aspects are discussed next.

1. Active constraints
   If one knew a priori the constraints that are active at the plant optimum, this knowledge could be used to simplify the solution to the RTO problem. In this study, for instance, the two constraints are active at the optimum. Since there are two decision variables, one could reach the optimum without explicit optimization simply by adjusting the two decision variables to activate the two constraints.

However, we assume here that the set of active constraints at the optimum is unknown, which corresponds to the assumption made in [137]. This is the case when there are significant changes in operating conditions or economic environment. Furthermore, even when the set of active constraints is known, the number of decision variables may be larger than the number of active constraints. In that case, explicit optimization relying on plant steady state is still necessary to find the optimal values of the unconstrained decision variables.

2. RTO versus model-based optimization
   For real-time optimization, a standard constrained optimization algorithm that implements an active set method, namely, the *fmincon* active set algorithm from MATLAB, is used here. There is an important difference when an optimization algorithm is used for RTO or for model-based optimization. In RTO, the values of the cost and constraints stem from plant measurements, whereas, in model-based optimization, these values are computed using the model. For RTO algorithms that use gradient information, the gradients need to be estimated experimentally via finite-difference or similar methods. Then, in both RTO and model-based optimization, the gradients are used to estimate the Hessian matrix. Since a reliable estimate of the Hessian is needed to compute acceptable step lengths and directions, the gradient estimates at each iteration must be both accurate and precise, that is, the error due to truncation and measurement noise must be small.

7.5.3.3 Simulated real-time optimization

The real-time optimization problem formulated above is simulated using first $\bar{n}_A^s$ and $\bar{n}_B^s$ as decision variables (case of controlled plant), and then $\bar{F}_A$ and $\bar{F}_B$ (open-loop plant).

1. RTO results with $\bar{n}_A^s$ and $\bar{n}_B^s$ as decision variables (controlled plant)
   Figures 7.7, 7.8 and 7.9 illustrate the RTO performance using $\bar{n}_A^s$ and $\bar{n}_B^s$ as decision variables. The scheme reaches the plant optimum after 8 iterations, while remaining (nearly) feasible. Each blue circle represents one plant run (that is, one plant operation between two successive steady states) in the space of decision variables, while the blue line corresponds to the progress of the RTO algorithm, starting from the initial point $(\bar{n}_A^s, \bar{n}_B^s) = (204.4, 51.1)$ mol. Note that three plant runs are necessary for each RTO iteration, namely, one run with the nominal values of the decision variables and two additional runs (one for each decision variable) to compute the gradients via finite differences. Hence, most of the blue circles do not coincide with the blue line since they correspond to points that are necessary to compute gradients via finite differences, while the blue line represents only the nominal points. The step away from each nominal point to compute the gradient with respect to a decision variable corresponds to 2.5% of the initial value of that decision variable. Furthermore, these perturbations are made in the direction of lower values of $\bar{n}_A^s$ and $\bar{n}_B^s$, because this direction is known to represent a smaller risk of constraint violation. Gradient estimation via finite differences is preferred for this RTO algorithm because an alternative gradient estimation

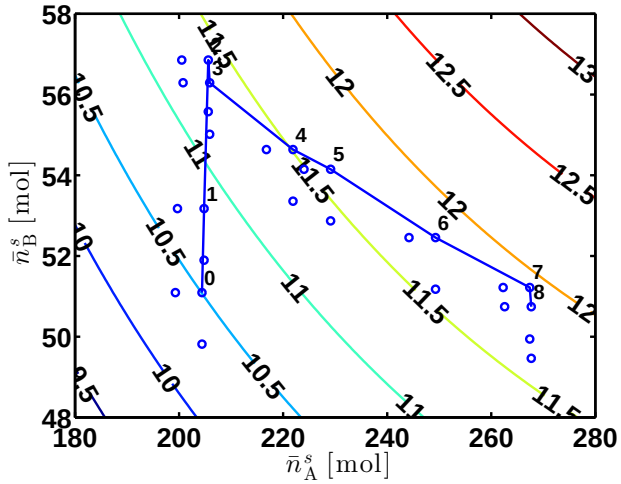

Figure 7.7 – Evolution of the objective function $\phi(\bar{n}_\mathrm{A}^s, \bar{n}_\mathrm{B}^s)$ over the RTO iterations.

based on previously visited points would either require smaller steps between iterations or result in large truncation error and inaccurate gradient estimates. Moreover, since the gradients are also used in the estimation of the Hessian matrix through a rank-one update based on the BFGS algorithm, it is recommended for the sake of accuracy not to use another rank-one update for gradient estimation such as the one used in the dual optimization approach [140].

Figure 7.10 shows a representative plant run (transient operation) for specific values of the decision variables $\bar{n}_\mathrm{A}^s$ and $\bar{n}_\mathrm{B}^s$. The top row of the figure shows the time profiles of the CVs, namely, $Q(t)$, $n_\mathrm{A}(t)$ and $n_\mathrm{B}(t)$. The second row shows the MVs $q_{ex}(t)$, $F_\mathrm{A}(t)$ and $F_\mathrm{B}(t)$. The next two rows represent the reaction rates $r_{v,1}(t)$ and $r_{v,2}(t)$, the jacket and reactor temperatures $T_j(t)$ and $T(t)$, and the numbers of moles $n_\mathrm{C}(t)$ and $n_\mathrm{D}(t)$. The time needed to reach the steady states $\bar{n}_\mathrm{A}$ and $\bar{n}_\mathrm{B}$ and estimate the reaction rates $\bar{r}_{v,1}$ and $\bar{r}_{v,2}$ is 16 min. The first 6 min are required for the CVs to converge to the setpoints $\bar{n}_\mathrm{A}^s$ and $\bar{n}_\mathrm{B}^s$. The true values of $n_\mathrm{A}(t)$ and $n_\mathrm{B}(t)$ in green converge quickly to their setpoints in red. However, one also observes that, during these 6 min, the variability of $F_\mathrm{A}(t)$ and $F_\mathrm{B}(t)$ is quite large, which in turn causes large variability in the estimated reaction rates. Hence, in the following 10 min, the controller gains are decreased to reduce the variability of the MVs and allow a more precise estimation of the reaction rates. At the end of the plant run, the window size of the convolution filter used for measurement-based rate estimation is increased from 3 to 10 min to obtain very precise values of the rate estimates. Then, the values of the MVs $\bar{F}_\mathrm{A}$ and $\bar{F}_\mathrm{B}$ that are used for evaluating the cost and constraints are computed from the reaction-rate estimates $\hat{\bar{r}}_{v,1}$ and $\hat{\bar{r}}_{v,2}$.

It is seen that one needs 10 min after the convergence of the CVs to be able to infer the cost and constraints with high precision. This high precision of the MVs and rate estimates is needed because the gradient estimation is highly sensitive to measurement

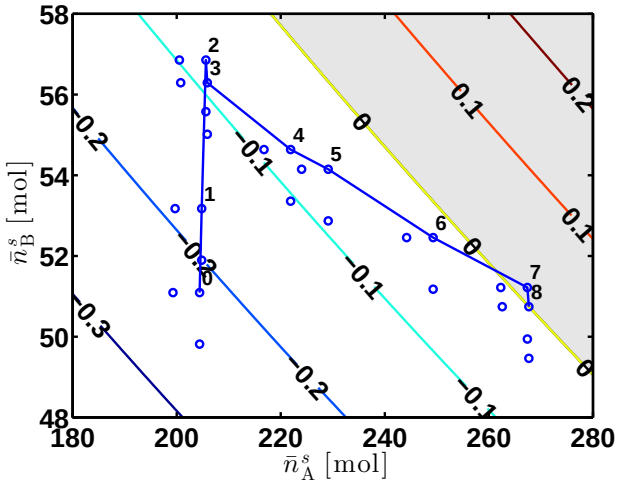

Figure 7.8 – Evolution of the constraint function $g_1(\bar{n}_{\mathrm{A}}^{s}, \bar{n}_{\mathrm{B}}^{s})$ over the RTO iterations (the shaded area is infeasible).

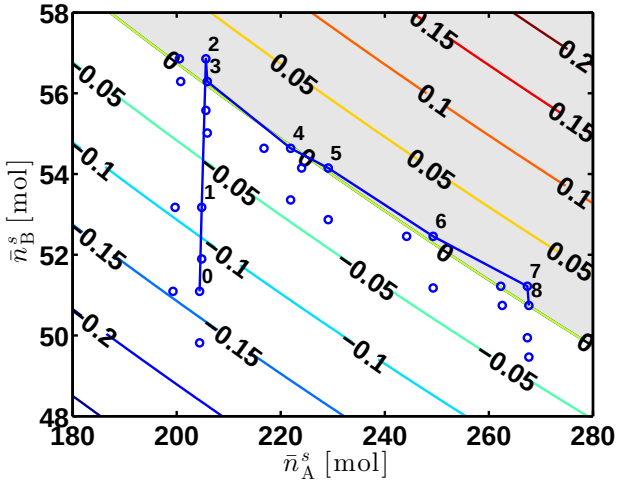

Figure 7.9 – Evolution of the constraint function $g_2(\bar{n}_{\mathrm{A}}^{s}, \bar{n}_{\mathrm{B}}^{s})$ over the RTO iterations (the shaded area is infeasible).

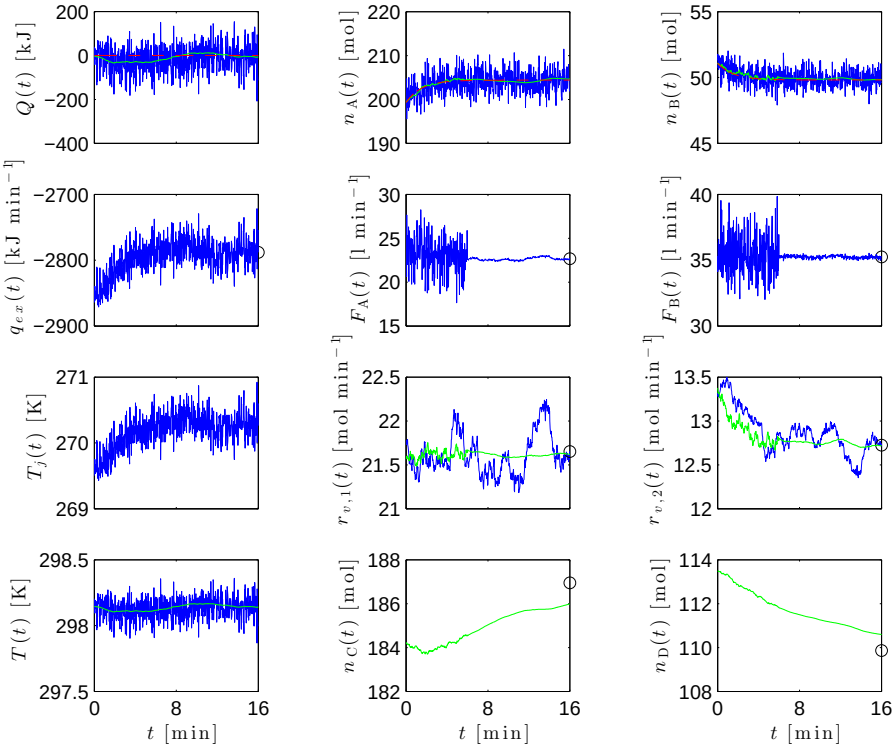

Figure 7.10 – Time profiles of the CVs (top row), the MVs (second row), the reaction rates, the temperatures $T_j(t)$ and $T(t)$, and the slow states $n_C(t)$ and $n_D(t)$ for a representative transient operation with specified values of $\bar{n}_A^s$ and $\bar{n}_B^s$. Blue lines represent measured, manipulated or estimated process values; black circles represent estimated steady-state values; green lines represent true (simulated) values; and dashed red lines represent setpoints.

noise. Since the gradients are used in the estimation of the Hessian matrix, the gradient estimates must be rather precise. Ultimately, if the estimated gradients and Hessian are not sufficiently precise, the optimization algorithm will not reach plant optimality.
For example, consider the hypothetical situation where the optimization algorithm has access to the true values of the reaction rates and the inlet flowrates corrupted with a small amount of zero-mean Gaussian noise (standard deviation of 0.4% for reaction rates and 0.04% for inlet flowrates). The RTO algorithm would stop prematurely as soon as one of the constraints becomes active, thus yielding a suboptimal solution (results not shown). This fact demonstrates how important it is to measure the cost and constraints with high precision, particularly so when the cost and constraint gradients are nearly parallel as in this example (as can be inferred from the contour lines in Figures 7.7, 7.8 and 7.9). Since, in this study, one can compute analytically both the variance of the rate estimates from Eq. (5.29) and the variance of the steady-state estimates from Eq. (7.29), one can also compute the variance of the cost and constraint gradients. This fact can be used to adjust the time needed to estimate the steady state such that a specific target for the variance of the cost and constraint gradients is reached.
On the other hand, the fact that the cost and constraint gradients are nearly parallel also implies that the cost does not improve much when one of the constraints becomes active. Let us imagine that the RTO algorithm stops as soon as one of the constraints becomes active. Then, a slightly suboptimal but relatively good cost value is obtained (11.3 mol l^{-1} min^{-1}, slightly lower than the optimal value of 11.8 mol l^{-1} min^{-1}, but clearly better than the initial value of 10.5 mol l^{-1} min^{-1}).
We assumed here that the rate model is unknown and no model-based Hessian is available, which calls for a low noise level or a relatively long waiting time to obtain steady-state estimates with high precision. In practice, however, it may be unrealistic to obtain such a high precision, and one may have to accept some optimality loss. Another possible strategy would consist in (i) having shorter runs when the constraints are not active and thus high precision is not needed, and (ii) increasing the run length when higher precision is needed due to active constraints.

2. RTO results with $\bar{F}_A$ and $\bar{F}_B$ as decision variables (open-loop plant)
Figures 7.11, 7.12 and 7.13 demonstrate that RTO using $\bar{F}_A$ and $\bar{F}_B$ as decision variables and starting from the initial point $(\bar{F}_A, \bar{F}_B) = (23.3, 36.7)$ l/min converges to plant optimality after 8 iterations as well. Again, three plant runs are necessary for each RTO iteration to estimate the gradients. In this particular problem, the cost and constraint gradients are less parallel, which implies that this case does not require as much precision in the gradients. In contrast to the previous case, in which $\bar{n}^s_A$ and $\bar{n}^s_B$ are used as decision variables, only the steady-state concentrations of C and D are measured here. However, one observes in Figure 7.14 that 48 min are necessary to reach the plant steady state and obtain the measurements needed to compute the cost and constraints. Within the same lapse of time, RTO using $\bar{n}^s_A$ and $\bar{n}^s_B$ as decision variables would have completed one entire iteration, that is, three plant runs!

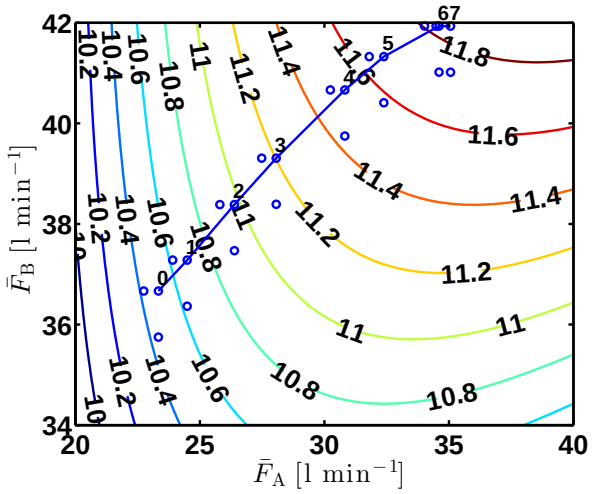

Figure 7.11 – Evolution of the objective function $\phi(\bar{F}_A, \bar{F}_B)$ over the RTO iterations.

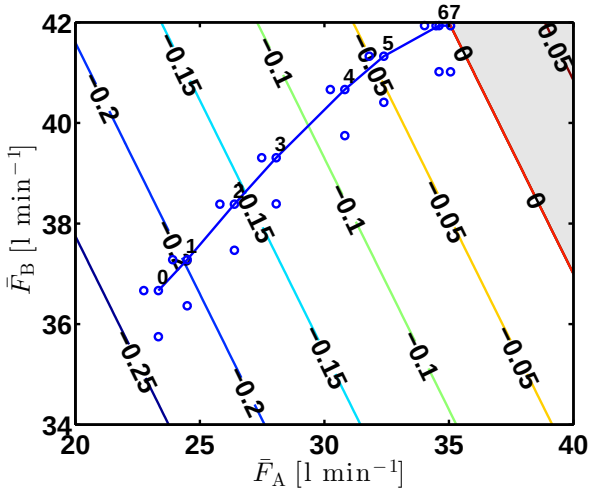

Figure 7.12 – Evolution of the constraint function $g_1(\bar{F}_A, \bar{F}_B)$ over the RTO iterations (the shaded area is infeasible).

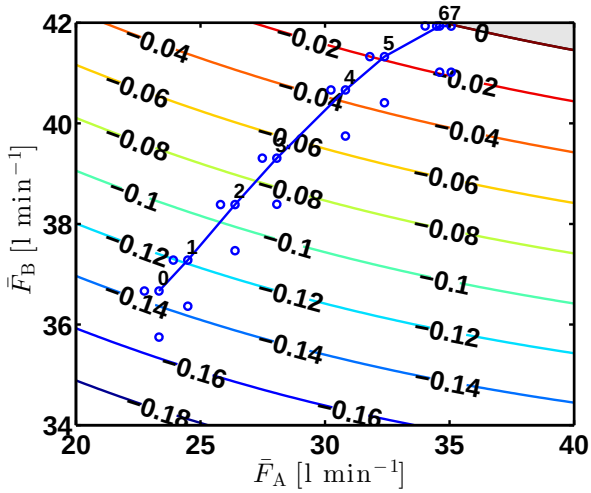

Figure 7.13 – Evolution of the constraint function $g_2(\bar{F}_{\mathrm{A}}, \bar{F}_{\mathrm{B}})$ over the RTO iterations (the shaded area is infeasible).

7.6 Conclusion

This chapter has presented a novel method that uses feedback control and measurement-based rate estimation to estimate the plant steady state quickly, that is, before the plant reaches steady state. This approach is possible for systems with a particular structure, namely, when some of the states do not affect the remaining states. In the context of real-time optimization, this implies that each iteration takes less time, which means that the time needed to drive the plant to optimality will be shorter.

The approach that has been presented includes the following ideas:

- One identifies a certain number of states that can be driven relatively quickly to steady state by manipulating appropriate inputs via feedback control. Note that this time to steady state may be much shorter than the time needed for the open-loop plant to reach steady state.
- Then, the cost and constraint functions of the RTO problem are reformulated so as to be expressed in terms of the fast (controlled) states. This reformulation is always possible, and it typically involves certain rates that depend only on fast states.
- However, since this approach is meant to be data-driven and not model-based, the reaction rates are estimated as time signals from output measurements, that is, without the use of rate models.
- The rates can be estimated as soon as their steady-state values have been reached, which avoids having to drive the slow states to steady state.
- The decision variables of the RTO problem correspond to setpoints of the controlled plant. Each time the decision variables are changed, feedback control drives the variables used in the computation of the cost and constraints toward their steady-state

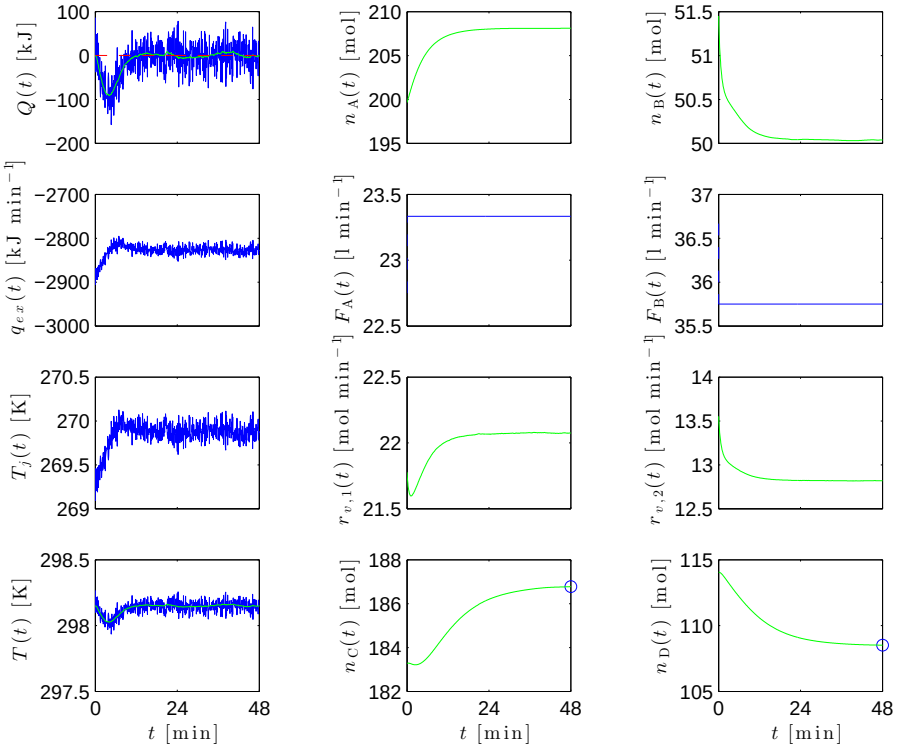

Figure 7.14 – Time profiles of the CV $Q(t)$, the MV $q_{ex}(t)$, the fast states $n_A(t)$ and $n_B(t)$, the inlet flowrates, the reaction rates, the temperatures $T_j(t)$ and $T(t)$, and the slow states $n_C(t)$ and $n_D(t)$ for a representative transient operation with specified values of $\bar{F}_A$ and $\bar{F}_B$. Blue lines represent measured, manipulated or estimated process values; blue circles represent measured steady-state values of the slow states; green lines represent true (simulated) values; and dashed red lines represent setpoints.

values in the shortest possible time.

Currently, the main limitation of this approach is its sensitivity to noise. This is particularly evident when the approach is applied to model-free static RTO since the use of a data-driven optimization algorithm restricts the admissible amount of noise in the steady-state estimates. The effect of noise would be less important if one waited for the plant to settle to steady state, because one would be able to apply noise reduction techniques that are particularly suited to constant signals. However, the time reduction inherent to the approach presented in this chapter provides a strong incentive to overcome these difficulties. Hence, it would be useful to investigate the use of alternative methods for feedback control, measurement-based rate estimation and real-time optimization to deal specifically with the issue of noise, while maintaining or even reducing the time needed to estimate the plant steady state. For example, with regard to real-time optimization, one could use algorithms that take advantage of the availability of an approximate model to reduce the detrimental effect of noise via the use of a model-based Hessian matrix. Note that this is possible even when the rate models are uncertain and the model-free techniques presented in this chapter are used for rate estimation, feedback control and steady-state estimation.

The various steps of the approach, namely, measurement-based rate estimation, feedback control, and optimization, require some parameters that need to be tuned appropriately. However, for many of these parameters, it is unclear how to choose or tune them. This tuning task appears to be challenging due to the coupling of the effects of the various parameters. Hence, the investigation of parameter tuning would be quite useful toward the successful implementation of these methods in practice.

In summary, this chapter has presented an approach that combines the concepts of rate estimation and feedback control to speed up the estimation of plant steady state. The ability to estimate steady-state values quickly is very relevant in the context of static RTO. If successfully implemented, this approach may lead to more flexible and adaptive operation of continuous processes. It is also expected that this chapter will trigger more research on the topic of fast steady-state estimation for dynamical systems.

8 Dynamic Optimization via Parsimonious Input Parameterization

Part of this chapter is adapted from the postprint of the following article [141]:

D. Rodrigues and D. Bonvin. Parsimonious input parameterization for dynamic optimization problems. *Comput. Aided Chem. Eng.*, 44:769–774, 2018.

Link: http://doi.org/10.1016/B978-0-444-64241-7.50123-3.

The author of this thesis contributed to that article by developing the main novel ideas, implementing the simulations, and writing a significant part of the text. Hence, the author retains the right to include the article in this thesis since it is not published commercially and the journal is referenced as the original source.

8.1 Introduction

In the case of continuous processes operated at steady state, the optimization problems are formulated with time-independent decision variables that represent the steady state of the process to be optimized. These problems are typically called static optimization problems, due to the static nature of the variables in the problem. Even for large-scale processes, efficient optimization algorithms have been developed, which allow computing an optimal steady state of the model of complex processes with relatively low computational effort [142].

However, in the case of batch processes that are not operated at steady state, the optimization problems are more complex since they are infinite-dimensional, that is, involving decision variables that represent time-varying input trajectories over a certain time horizon. The optimization of these input trajectories results in the so-called dynamic optimization problems since they correspond to processes of dynamic nature, where steady state is not reached. In these problems, also known as optimal control problems, in addition to the economic cost and operational constraints at the end of the time horizon, there exist path constraints along the trajectory as well, which also make these problems more complex [143]. For these problems, specialized techniques have been developed, which can be di-

vided into two main categories: indirect and direct methods. Indirect methods attempt to solve the problem by seeking a solution to the necessary conditions of optimality of the dynamic optimization problem, using for example Pontryagin's Maximum Principle [144, 145] or the Hamilton-Jacobi-Bellman equation [143, 146]. On the other hand, direct methods reformulate the original infinite-dimensional problem as a finite-dimensional problem via discretization. In direct sequential methods, the inputs are discretized [147, 148], whereas in direct simultaneous methods, both the inputs and states are discretized [149, 150]. Direct multiple shooting represents an intermediate alternative, whereby the states are discretized only at some control stage times [151, 152].

Dynamic optimization methods that rely on local numerical optimization are well established [153]. However, the local optima attained by these optimization algorithms may be suboptimal with respect to the global optimum by a significant margin. Although these methods typically attain local optimality, they could be extended to global optimality. However, the worst-case complexity scales exponentially with the number of decision variables [154]. This implies that only problems with a relatively low number of decision variables can be solved to global optimality, which represents a major hindrance to the use of global optimization for complex optimization problems since the computational effort becomes prohibitive. For example, if one uses direct sequential methods, the number of decision variables is equal to the number of input parameters, which is proportional to the number of intervals of the piecewise-constant input parameterization often used by these methods [155]. Hence, the use of direct methods for global optimization either calls for a rather coarse input parameterization or results in intractable problems.

An apparent way to avoid these difficulties is to use an input parameterization that can approximate the optimal inputs well with a limited number of parameters. This chapter proposes a *parsimonious* input parameterization, whereby the parameters correspond to (i) switching times between arcs, and (ii) a few parameters used to describe sensitivity-seeking arcs. This parameterization helps reduce the number of decision variables of the optimization problem, resulting in a much smaller number of decision variables than traditional direct simultaneous or direct sequential methods. A similar parameterization has been applied to the dynamic optimization of switched systems [156]. However, to the author's knowledge, it has not been proposed for problems with inequality constraints or in the context of global optimization.

Hence, this chapter presents a way to move toward finding global solutions to a generic class of dynamic optimization problems by applying the concept of parsimonious input parameterization. The parsimonious input parameterization is useful not only for finding global solutions to dynamic optimization problems, but also for dynamic real-time optimization in the presence of plant-model mismatch, which also requires a small number of decision variables. This document also shows how one can apply this method in the context of dynamic optimization of batch, semi-batch and continuous reactors.

The method is divided in two parts. Firstly, after presenting the problem formulation in Section 8.2, the optimal control laws are generated in Section 8.3 for all the possible types

of arcs that may occur in the optimal solution, and a finite set of plausible arc sequences is postulated from these types of arcs. In the case of batch, semi-batch or continuous reactors, one takes advantage of the concept of extents to convert the model of any of these reactors into a general framework, which allows the symbolic computation of adjoint-free optimal control laws in a uniform and systematic fashion. In the second part in Section 8.4, each arc sequence is described by a small number of parameters that include switching times and initial conditions for the sensitivity-seeking arcs. These arcs may be parsimoniously described by either cubic splines with few parameters or optimal control laws generated via symbolic computation. Then, the parsimonious input parameterization approach is applied to find the correct arc sequence. For each arc sequence, the optimal parameter values are computed as the solution to a numerical optimization problem that can also be used to check whether the resulting input trajectory satisfies the necessary conditions of optimality given by the Pontryagin's maximum principle. The reduction in the number of decision variables is such that the problem is often amenable to global optimization. Then, if a global solution is found for each arc sequence, the arc sequence with the best optimal cost will be globally optimal. The procedure is illustrated in Section 8.5 via the optimization of simulated semi-batch reactors and batch distillation columns. Finally, Section 8.6 concludes the chapter.

8.2 Problem Formulation

The class of dynamic optimization problems considered in this chapter is formulated in the Mayer form as

$$\min_{\mathbf{u}(\cdot),t_f} \quad \mathscr{J}\left(\mathbf{u}(\cdot),t_f\right)=\phi\left(\mathbf{x}(t_f),t_f\right), \tag{8.1a}$$

$$\text{s.t.} \quad \mathscr{O}\left(\mathbf{u}(\cdot),t_f\right)=\boldsymbol{\omega}\left(\mathbf{x}(t_f),t_f\right)=\mathbf{0}_{n_\omega}, \tag{8.1b}$$

$$\mathscr{T}\left(\mathbf{u}(\cdot),t_f\right)=\boldsymbol{\psi}\left(\mathbf{x}(t_f),t_f\right)\leq\mathbf{0}_{n_\psi}, \tag{8.1c}$$

$$\dot{\mathbf{x}}(t)=\mathbf{f}\big(\mathbf{x}(t),\mathbf{u}(t)\big), \quad \mathbf{x}(t_0)=\mathbf{x}_0, \tag{8.1d}$$

$$\mathbf{g}\big(\mathbf{x}(t),\mathbf{u}(t)\big)\leq\mathbf{0}_{n_g}, \tag{8.1e}$$

$$\mathbf{h}\big(\mathbf{x}(t)\big)\leq\mathbf{0}_{n_h}, \tag{8.1f}$$

where t_0 is the initial time, $t_f\in\left[t_0,t_{up}\right]$ is the finite final time, with t_{up} being an upper bound for t_f, $\mathbf{u}(t)$ is the n_u-dimensional vector of piecewise-continuous inputs for all $t\in\left[t_0,t_f\right)$ with trajectory $\mathbf{u}(\cdot)$, $\mathbf{x}(t)$ is the n_x-dimensional vector of piecewise-continuously differentiable states for all $t\in\left[t_0,t_f\right)$, $\mathbf{f}(\mathbf{x},\mathbf{u})$ and $\mathbf{g}(\mathbf{x},\mathbf{u})$ are an n_x-dimensional function and an n_g-dimensional function, smooth for all $(\mathbf{x},\mathbf{u})\in\mathbb{R}^{n_x}\times\mathbb{R}^{n_u}$, $\mathbf{h}(\mathbf{x})$ is an n_h-dimensional function, smooth for all $\mathbf{x}\in\mathbb{R}^{n_x}$, and $\phi(\mathbf{x},t)$, $\boldsymbol{\omega}(\mathbf{x},t)$, and $\boldsymbol{\psi}(\mathbf{x},t)$ are a scalar function, an n_ω-dimensional function, and an n_ψ-dimensional function, smooth for all $(\mathbf{x},t)\in\mathbb{R}^{n_x}\times[t_0,t_{up}]$. Moreover, it is assumed that the functions $\mathbf{g}(\mathbf{x},\mathbf{u})$ and $\mathbf{h}^{(1)}(\mathbf{x},\mathbf{u}):=$

$\dot{\mathbf{h}}(\mathbf{x}) = \frac{\partial \mathbf{h}}{\partial \mathbf{x}}(\mathbf{x})\mathbf{f}(\mathbf{x},\mathbf{u})$ depend explicitly on $\mathbf{u}$, which is equivalent to the conditions

$$\frac{\partial g_k}{\partial \mathbf{u}}(\mathbf{x},\mathbf{u})^{\mathrm{T}} \neq \mathbf{0}_{n_u}, \quad \forall k = 1,\ldots,n_g, \tag{8.2a}$$

$$\frac{\partial h_k^{(1)}}{\partial \mathbf{u}}(\mathbf{x},\mathbf{u})^{\mathrm{T}} \neq \mathbf{0}_{n_u}, \quad \forall k = 1,\ldots,n_h. \tag{8.2b}$$

Note that a time-invariant problem formulation is considered in Problem (8.1).

8.3 Adjoint-free Optimal Control Laws

This section presents the method used to compute *adjoint-free* optimal control laws for a generic system. In addition, the mass and heat balances for batch, semi-batch and continuous reactors (or any reactors whose inverse of the residence time is constant) are formulated using the concept of extents, and it is shown how one can combine these elements in a way that allows the automatic computation of optimal control laws for these reactors.

8.3.1 Analytical computation of adjoint-free optimal control laws

This subsection presents the method of computation of adjoint-free optimal control laws introduced in [157], whereas the next subsection shows how it can be applied in the case of batch, semi-batch and continuous reactors through the use of the concept of extents.

Most often, the optimal input trajectories that correspond to the solution to any given optimal control problem consist of a finite number of arcs. For a given arc, each optimal input is determined by either an active path constraint or a single condition that expresses physical compromises and trade-offs and depends exclusively on the system dynamics, provided that the functionals $\mathscr{J}\left(\mathbf{u}(\cdot),t_f\right)$, $\mathscr{O}\left(\mathbf{u}(\cdot),t_f\right)$ and $\mathscr{T}\left(\mathbf{u}(\cdot),t_f\right)$ are written in the Mayer form.[1] In both cases, the optimal input or one of its time derivatives can be written as a function of the states, the inputs and the time derivatives of the inputs, with no dependence on any adjoint variables. Moreover, the resulting optimal control laws (but not necessarily the control values) are independent of the initial conditions and the terminal constraints of the problem [157].

Let the input u_j be an element of $\mathbf{u}$, for some $j = 1,\ldots,n_u$.[2] The control laws express

[1] Note that some of the functionals $\mathscr{J}\left(\mathbf{u}(\cdot),t_f\right)$, $\mathscr{O}\left(\mathbf{u}(\cdot),t_f\right)$ and $\mathscr{T}\left(\mathbf{u}(\cdot),t_f\right)$ may depend on integrals of functions of the states and inputs. In that case, those functionals are written in the Bolza form and not in the Mayer form. For example, for the cost functional $\mathscr{J}\left(\mathbf{u}(\cdot),t_f\right)$, if there are scalar functions $\check{\phi}\left(\mathbf{x}(t_f),t_f\right)$ and $l_{\mathscr{J}}\left(\mathbf{x}(t),\mathbf{u}(t)\right)$ such that $\mathscr{J}\left(\mathbf{u}(\cdot),t_f\right) = \check{\phi}\left(\mathbf{x}(t_f),t_f\right) + \int_{t_0}^{t_f} l_{\mathscr{J}}\left(\mathbf{x}(t),\mathbf{u}(t)\right)\mathrm{d}t$, then the functional $\mathscr{J}\left(\mathbf{u}(\cdot),t_f\right)$ is in the Bolza form. The conversion to the Mayer form typically requires the inclusion of a new state with derivative $l_{\mathscr{J}}\left(\mathbf{x}(t),\mathbf{u}(t)\right)$. However, if the functionals in the Bolza form depend on integrals of linear functions of the derivatives $\mathbf{f}\left(\mathbf{x}(t),\mathbf{u}(t)\right)$ of the states, they can easily be converted to the Mayer form. For example, if there is a scalar function $\check{\phi}\left(\mathbf{x}(t_f),t_f\right)$ and a vector $\mathbf{l}_{\mathscr{J}}$ such that $\mathscr{J}\left(\mathbf{u}(\cdot),t_f\right) = \check{\phi}\left(\mathbf{x}(t_f),t_f\right) + \mathbf{l}_{\mathscr{J}}^{\mathrm{T}} \int_{t_0}^{t_f} \mathbf{f}\left(\mathbf{x}(t),\mathbf{u}(t)\right)\mathrm{d}t$, then the functional $\mathscr{J}\left(\mathbf{u}(\cdot),t_f\right)$ can simply be written as $\mathscr{J}\left(\mathbf{u}(\cdot),t_f\right) = \phi\left(\mathbf{x}(t_f),t_f\right) = \check{\phi}\left(\mathbf{x}(t_f),t_f\right) + \mathbf{l}_{\mathscr{J}}^{\mathrm{T}}\left(\mathbf{x}(t_f) - \mathbf{x}_0\right)$.

[2] For the sake of simplicity, the dependence of the states $\mathbf{x}$, the inputs $\mathbf{u}$ and their time derivatives on the time

the optimal input u_j or one of its time derivatives in terms of the states and possibly the inputs and their time derivatives, thus resulting in an *adjoint-free* optimal control law c_j. Each input arc is of one of the following three types [157]:

- Arc type 1: If the optimal input u_j is determined by the active mixed path constraint $g_k(\mathbf{x},\mathbf{u}) \leq 0$, for some $k = 1,\ldots,n_g$, then the control law

$$u_j = c_j(\mathbf{x},\mathbf{u}) \tag{8.3}$$

  enforces

$$g_k(\mathbf{x},\mathbf{u}) = 0. \tag{8.4}$$

- Arc type 2: If the optimal input u_j is determined by the active pure-state path constraint $h_k(\mathbf{x}) \leq 0$, for some $k = 1,\ldots,n_h$, then the control law

$$u_j = c_j(\mathbf{x},\mathbf{u}) \tag{8.5}$$

  enforces

$$h_k^{(1)}(\mathbf{x},\mathbf{u}) = 0. \tag{8.6}$$

- Arc type 3: If the optimal input u_j is not determined by any active path constraints, then the control law

$$u_j^{(\xi_j)} = c_j(\mathbf{x}, u_1^{(\xi_1-1)},\ldots,u_1,\ldots,u_{n_u}^{(\xi_{n_u}-1)},\ldots,u_{n_u}) \tag{8.7}$$

  enforces

$$\det\left(\mathscr{M}_j\right) = 0. \tag{8.8}$$

  Let $\mathbf{x}^{u_j}$ be the ρ_j states that can be reached by manipulating u_j, with dynamics

$$\dot{\mathbf{x}}^{u_j} = \mathbf{f}^{u_j}(\mathbf{x},\mathbf{u}). \tag{8.9}$$

  Then, one can construct the $(\rho_j \times \rho_j)$ matrix

$$\mathscr{M}_j := \left[\frac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u}) \;\; \Delta_j\frac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u}) \;\; \cdots \;\; \Delta_j^{\rho_j-1}\frac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u})\right], \tag{8.10}$$

t is omitted in all the text concerning analytical computation of adjoint-free optimal control laws.

using symbolic computations and the operators $\Delta_j, \ldots, \Delta_j^{\rho_j - 1}$ defined as

$$\Delta_j^l \mathbf{v} := \begin{cases} \dfrac{\partial \mathbf{v}}{\partial \mathbf{x}} \mathbf{f}(\mathbf{x}, \mathbf{u}) - \dfrac{\partial \mathbf{f}^{u_j}}{\partial \mathbf{x}^{u_j}}(\mathbf{x}, \mathbf{u}) \mathbf{v} + \displaystyle\sum_{n=0}^{\infty} \frac{\partial \mathbf{v}}{\partial \mathbf{u}^{(n)}} \mathbf{u}^{(n+1)}, & l = 1 \\ \Delta_j \left(\Delta_j^{l-1} \mathbf{v} \right), & l = 2, \ldots, \rho_j - 1 \end{cases}, \quad (8.11)$$

for any vector field $\mathbf{v}$ of dimension ρ_j.
However, the input u_j and its time derivatives may not appear explicitly in the function $\det\left(\mathscr{M}_j\right)$. Hence, as a general approach to find the optimal input u_j when it is not determined by active path constraints, the function $\det\left(\mathscr{M}_j\right)$ is subject to time differentiation until u_j or one of its time derivatives appears in $\frac{\mathrm{d}^{r_j}}{\mathrm{d}t^{r_j}}\left(\det\left(\mathscr{M}_j\right)\right)$, for some r_j. Let $u_j^{(\xi_j)}$ be the highest-order time derivative of u_j that appears in $\frac{\mathrm{d}^{r_j}}{\mathrm{d}t^{r_j}}\left(\det\left(\mathscr{M}_j\right)\right)$. Then, the control law enforces

$$\frac{\mathrm{d}^{r_j}}{\mathrm{d}t^{r_j}}\left(\det\left(\mathscr{M}_j\right)\right) = 0. \quad (8.12)$$

If u_j and its time derivatives do not appear in $\frac{\mathrm{d}^{r_j}}{\mathrm{d}t^{r_j}}\left(\det\left(\mathscr{M}_j\right)\right)$ for any r_j, then the optimal input u_j is never of this type, and it is always determined by an active path constraint according to one of the other types. For example, if a time derivative of $\det\left(\mathscr{M}_j\right)$ is identically equal to zero while u_j and its time derivatives do not appear in any of the lower-order time derivatives of $\det\left(\mathscr{M}_j\right)$, it is possible to guarantee that u_j and its time derivatives will not appear in $\frac{\mathrm{d}^{r_j}}{\mathrm{d}t^{r_j}}\left(\det\left(\mathscr{M}_j\right)\right)$ for any r_j.
Note that, if there are inputs that depend on each other, one may need to solve a system of equations to find the optimal control law for each input.

In the remainder, the input arcs of types 1 and 2 are labeled *constraint-seeking*, while the input arcs of type 3 are *sensitivity-seeking*. Note that switching between arcs can happen any time, except for the switching to arcs of type 2 that can only occur when the states $\mathbf{x}$ satisfy $h_k(\mathbf{x}) = 0$, for some $k = 1, \ldots, n_h$.

8.3.2 Computation of adjoint-free optimal control laws for reactors using extents

Let us consider a homogeneous reactor with R independent reactions and p independent inlets, where $\mathbf{u}_{in}(t)$ is the p-dimensional vector of inlet mass flowrates, $q_{ex}(t)$ is the exchanged heat power, and the inverse of the residence time ω is constant. This reactor may be either a batch or semi-batch reactor without outlet ($\omega = 0$) or a continuous stirred-tank reactor (CSTR) with constant outlet volumetric flowrate (constant $\omega > 0$) where the effect of the initial conditions has vanished (after sufficiently long operation). The numbers of

moles $\mathbf{n}(t)$ and the heat $Q(t)$ in this reactor are equal to the linear combinations of extents

$$\begin{bmatrix}\mathbf{n}(t)\\ Q(t)\end{bmatrix} = \begin{bmatrix}\mathbf{N}^{\mathrm{T}}\\ -\Delta\mathbf{H}_r^{\mathrm{T}}\end{bmatrix}\mathbf{x}_r(t) + \begin{bmatrix}\mathbf{W}_{in}\\ \check{\mathbf{T}}_{in}^{\mathrm{T}}\end{bmatrix}\mathbf{x}_{in}(t) + \begin{bmatrix}\mathbf{0}_S\\ 1\end{bmatrix}x_{ex}(t) + \begin{bmatrix}\mathbf{n}_0\\ Q_0\end{bmatrix}x_{ic}, \tag{8.13}$$

where $\mathbf{n}_0$ is the S-dimensional vector of initial numbers of moles, Q_0 is the initial heat, $\mathbf{N}$ is the $R \times S$ stoichiometric matrix, $\Delta\mathbf{H}_r$ is the R-dimensional vector of enthalpies of reaction, $\mathbf{W}_{in}$ is the $S \times p$ inlet-composition matrix, $\check{\mathbf{T}}_{in}$ is the p-dimensional vector of inlet specific heats, $\mathbf{x}_r(t)$ is the R-dimensional vector of extents of reaction, $\mathbf{x}_{in}(t)$ is the p-dimensional vector of extents of inlet, $x_{ex}(t)$ is the extent of heat exchange, and x_{ic} is the extent of initial conditions, which is equal to 1 in a reactor without outlet ($\omega = 0$) and equal to 0 in a reactor with outlet (constant $\omega > 0$) where the effect of the initial conditions has vanished.

Note that Eq. (8.13) can easily be extended to the case of heterogeneous reactors whose inverse of the residence time in each phase is constant (in particular, heterogeneous batch and semi-batch reactors), by taking into account the numbers of moles and heats in the different phases and by appending the extents of mass transfer to the extents of reaction. However, for the sake of simplicity, this chapter considers the case of a homogeneous reactor.

Hence, the state vector of dimension $n_x := R + p + 1$ that represents this system is

$$\mathbf{x}(t) := \begin{bmatrix}\mathbf{x}_r(t)\\ \mathbf{x}_{in}(t)\\ x_{ex}(t)\end{bmatrix}, \tag{8.14}$$

whereas the input vector of dimension $n_u := p + 1$ is

$$\mathbf{u}(t) := \begin{bmatrix}\mathbf{u}_{in}(t)\\ q_{ex}(t)\end{bmatrix}. \tag{8.15}$$

The dynamic equations that describe the system can be written compactly as

$$\dot{\mathbf{x}}(t) = \mathbf{f}\big(\mathbf{x}(t), \mathbf{u}(t)\big), \quad \mathbf{x}(t_0) = \mathbf{x}_0, \tag{8.16}$$

by defining

$$\mathbf{f}\big(\mathbf{x}(t), \mathbf{u}(t)\big) := \begin{bmatrix}\mathbf{r}_v(t)\\ \mathbf{u}(t)\end{bmatrix} - \omega\mathbf{x}(t), \tag{8.17}$$

where $\mathbf{r}_v(t) := \upsilon\big(\mathbf{n}(t), Q(t)\big)\boldsymbol{\varphi}\big(\mathbf{n}(t), Q(t)\big)$, with $\upsilon(\mathbf{n}, Q)$ the volume and $\boldsymbol{\varphi}(\mathbf{n}, Q)$ the R-dimensional vector of reaction rates expressed as a function of the numbers of moles and heat, which depend on $\mathbf{x}(t)$ as shown in Eq. (8.13). Hence, this system is input-affine.

If the state x_j is the element of $\mathbf{x}$ such that

$$\dot{x}_j = f_j(\mathbf{x}, \mathbf{u}) := u_j - \omega x_j, \tag{8.18}$$

then it is possible to define the following vectors of dimension $\rho_j := R+1$:

$$\mathbf{x}^{u_j} := \begin{bmatrix} \mathbf{x}_r \\ x_j \end{bmatrix}, \tag{8.19}$$

$$\mathbf{f}^{u_j}(\mathbf{x},\mathbf{u}) := \begin{bmatrix} \mathbf{r}_v \\ u_j \end{bmatrix} - \omega \mathbf{x}^{u_j}. \tag{8.20}$$

Before analyzing particular reactor cases, let us define the state vector $\check{\mathbf{x}}_j$ as the complement of the state x_j (all the states $\mathbf{x}$ except x_j), and the vector $\check{\mathbf{f}}_j(\mathbf{x},\mathbf{u})$ as the corresponding complement of $f_j(\mathbf{x},\mathbf{u})$ (the right-hand side of the dynamic equations of all the states $\mathbf{x}$ except x_j).

For illustrative purposes, let us derive the expressions of the columns of $\mathscr{M}_j$ for the cases of 1 independent reaction ($\rho_j - 1 = R = 1$) and 2 independent reactions ($\rho_j - 1 = R = 2$):

$$\frac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u}) = \begin{bmatrix} \mathbf{0}_R \\ 1 \end{bmatrix}, \tag{8.21}$$

$$\begin{aligned}
\Delta_j \frac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u}) &= \frac{\partial}{\partial \mathbf{x}} \left(\frac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u}) \right) \mathbf{f}(\mathbf{x},\mathbf{u}) - \frac{\partial \mathbf{f}^{u_j}}{\partial \mathbf{x}^{u_j}}(\mathbf{x},\mathbf{u}) \frac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u}) \\
&\quad + \sum_{n=0}^{\infty} \frac{\partial}{\partial \mathbf{u}^{(n)}} \left(\frac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u}) \right) \mathbf{u}^{(n+1)} \\
&= \frac{\partial}{\partial \mathbf{x}} \left(\begin{bmatrix} \mathbf{0}_R \\ 1 \end{bmatrix} \right) \mathbf{f}(\mathbf{x},\mathbf{u}) - \frac{\partial}{\partial \mathbf{x}^{u_j}} \left(\begin{bmatrix} \mathbf{r}_v \\ u_j \end{bmatrix} - \omega \mathbf{x}^{u_j} \right) \begin{bmatrix} \mathbf{0}_R \\ 1 \end{bmatrix} \\
&\quad + \sum_{n=0}^{\infty} \frac{\partial}{\partial \mathbf{u}^{(n)}} \left(\begin{bmatrix} \mathbf{0}_R \\ 1 \end{bmatrix} \right) \mathbf{u}^{(n+1)} \\
&= - \left(\begin{bmatrix} \frac{\partial \mathbf{r}_v}{\partial \mathbf{x}_r} & \frac{\partial \mathbf{r}_v}{\partial x_j} \\ \mathbf{0}_R^{\mathrm{T}} & 0 \end{bmatrix} - \omega \mathbf{I}_{R+1} \right) \begin{bmatrix} \mathbf{0}_R \\ 1 \end{bmatrix} \\
&= \begin{bmatrix} -\frac{\partial \mathbf{r}_v}{\partial x_j} \\ \omega \end{bmatrix},
\end{aligned} \tag{8.22}$$

$$
\begin{aligned}
\Delta_j^2 \frac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u}) &= \frac{\partial}{\partial \mathbf{x}}\left(\Delta_j \frac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u})\right)\mathbf{f}(\mathbf{x},\mathbf{u}) - \frac{\partial \mathbf{f}^{u_j}}{\partial \mathbf{x}^{u_j}}(\mathbf{x},\mathbf{u})\Delta_j \frac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u}) \\
&\quad + \sum_{n=0}^{\infty} \frac{\partial}{\partial \mathbf{u}^{(n)}}\left(\Delta_j \frac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u})\right)\mathbf{u}^{(n+1)} \\
&= \frac{\partial}{\partial \mathbf{x}}\left(\begin{bmatrix} -\frac{\partial \mathbf{r}_v}{\partial x_j} \\ \omega \end{bmatrix}\right)\mathbf{f}(\mathbf{x},\mathbf{u}) - \frac{\partial}{\partial \mathbf{x}^{u_j}}\left(\begin{bmatrix} \mathbf{r}_v \\ u_j \end{bmatrix} - \omega \mathbf{x}^{u_j}\right)\begin{bmatrix} -\frac{\partial \mathbf{r}_v}{\partial x_j} \\ \omega \end{bmatrix} \\
&\quad + \sum_{n=0}^{\infty} \frac{\partial}{\partial \mathbf{u}^{(n)}}\left(\begin{bmatrix} -\frac{\partial \mathbf{r}_v}{\partial x_j} \\ \omega \end{bmatrix}\right)\mathbf{u}^{(n+1)} \\
&= -\begin{bmatrix} \frac{\partial}{\partial \check{\mathbf{x}}_j}\left(\frac{\partial \mathbf{r}_v}{\partial x_j}\right) \\ \mathbf{0}_{R+p}^{\mathrm{T}} \end{bmatrix}\check{\mathbf{f}}_j(\mathbf{x},\mathbf{u}) - \begin{bmatrix} \frac{\partial}{\partial x_j}\left(\frac{\partial \mathbf{r}_v}{\partial x_j}\right) \\ 0 \end{bmatrix}\left(u_j - \omega x_j\right) \\
&\quad - \left(\begin{bmatrix} \frac{\partial \mathbf{r}_v}{\partial \mathbf{x}_r} & \frac{\partial \mathbf{r}_v}{\partial x_j} \\ \mathbf{0}_R^{\mathrm{T}} & 0 \end{bmatrix} - \omega \mathbf{I}_{R+1}\right)\begin{bmatrix} -\frac{\partial \mathbf{r}_v}{\partial x_j} \\ \omega \end{bmatrix} \\
&= \begin{bmatrix} \left(\frac{\partial \mathbf{r}_v}{\partial \mathbf{x}_r} - 2\omega \mathbf{I}_R\right)\frac{\partial \mathbf{r}_v}{\partial x_j} - \frac{\partial}{\partial \check{\mathbf{x}}_j}\left(\frac{\partial \mathbf{r}_v}{\partial x_j}\right)\check{\mathbf{f}}_j(\mathbf{x},\mathbf{u}) \\ \omega^2 \end{bmatrix} \\
&\quad + \begin{bmatrix} -\frac{\partial}{\partial x_j}\left(\frac{\partial \mathbf{r}_v}{\partial x_j}\right)\left(u_j - \omega x_j\right) \\ 0 \end{bmatrix}.
\end{aligned} \tag{8.23}
$$

From the previous sequence, it becomes clear that, since this system is input-affine, the columns of $\mathscr{M}_j$ are polynomial functions of u_j and its time derivatives, which implies that $\det\left(\mathscr{M}_j\right)$ and its time derivatives are also polynomial functions of u_j and its time derivatives, resulting in a finite number of solutions that satisfy the condition in Eq. (8.12). Furthermore, there is a single solution that satisfies the condition in Eq. (8.12) if $\frac{\partial}{\partial u_j^{(\xi_j)}}\left(\frac{\mathrm{d}^{r_j}}{\mathrm{d}t^{r_j}}\left(\det\left(\mathscr{M}_j\right)\right)\right)$ is independent of $u_j^{(\xi_j)}$ and nonzero for any attainable values of $\mathbf{x}$. For example, in the context of reaction systems, this is the case when $\frac{\partial \det\left(\mathscr{M}_j\right)}{\partial u_j^{(R-2)}}$ or $\frac{\partial}{\partial u_j}\left(\frac{\mathrm{d}^{r_j}}{\mathrm{d}t^{r_j}}\left(\det\left(\mathscr{M}_j\right)\right)\right)$ is nonzero for any attainable values of $\mathbf{x}$, which occurs in many optimal control problems.

Hence, as shown in Appendix G.1, one can prove that:

1. For reactors with one independent reaction, when the optimal input u_j is not determined by any active path constraints, it is determined by the scalar function

$$
\frac{\mathrm{d}}{\mathrm{d}t}\left(\det\left(\mathscr{M}_j\right)\right) = \frac{\partial}{\partial \check{\mathbf{x}}_j}\left(\frac{\partial r_v}{\partial x_j}\right)\check{\mathbf{f}}_j(\mathbf{x},\mathbf{u}) + \frac{\partial}{\partial x_j}\left(\frac{\partial r_v}{\partial x_j}\right)\left(u_j - \omega x_j\right), \tag{8.24}
$$

since u_j and its time derivatives do not appear in

$$\det\left(\mathscr{M}_j\right) = \frac{\partial r_v}{\partial x_j}. \tag{8.25}$$

2. For reactors with two independent reactions, when the optimal input u_j is not determined by any active path constraints, it is determined by the scalar function

$$\begin{aligned}\det\left(\mathscr{M}_j\right) = \det\left(\left[\frac{\partial \mathbf{r}_v}{\partial x_j} \quad \frac{\partial}{\partial \check{\mathbf{x}}_j}\left(\frac{\partial \mathbf{r}_v}{\partial x_j}\right)\check{\mathbf{f}}_j(\mathbf{x},\mathbf{u}) - \left(\frac{\partial \mathbf{r}_v}{\partial \mathbf{x}_r} - 2\omega\mathbf{I}_R\right)\frac{\partial \mathbf{r}_v}{\partial x_j}\right]\right) \\ + \det\left(\left[\frac{\partial \mathbf{r}_v}{\partial x_j} \quad \frac{\partial}{\partial x_j}\left(\frac{\partial \mathbf{r}_v}{\partial x_j}\right)\right]\right)\left(u_j - \omega x_j\right).\end{aligned} \tag{8.26}$$

For any number of independent reactions, one can use symbolic computation software to compute the function $\det\left(\mathscr{M}_j\right)$ and its time derivatives automatically and to obtain the optimal input u_j or one of its time derivatives that satisfies the condition in Eq. (8.12) when the input is not determined by any active path constraints.

Note that the use of extents is essential here. The extents are needed to obtain the minimal number of states reached by u_j and a matrix $\mathscr{M}_j$ that loses full rank if and only if u_j is sensitivity-seeking, that is, if and only if u_j is described by an optimal control law. In other words, it would not be possible to achieve the same result with the numbers of moles and the heat as states of the optimal control problem.

The analytical approach for the computation of adjoint-free optimal control laws shown above is quite useful to get an analytical characterization of the constraint-seeking and sensitivity-seeking input arcs. However, when the number of reachable states ρ_j grows beyond 4 or 5 (that is, 3 or 4 independent reactions in reaction systems), the size and complexity of the matrix $\mathscr{M}_j$ may become intractable, which complicates the characterization of sensitivity-seeking arcs. Fortunately, many reaction systems can be described, or at least approximated very well, by a model with only a few independent reactions, which renders this analytical approach quite useful for many reaction systems. On the other hand, for other systems, including some reaction systems, a more practical approach may be needed. Nevertheless, it is desirable to retain the high level of accuracy provided by the analytical approach.

8.3.3 Approximation of adjoint-free optimal control laws using cubic splines

The idea is to replace the analytical characterization of sensitivity-seeking input arcs by a description of these arcs using cubic splines (that is, piecewise-cubic functions). Since the optimal input profiles in these arcs are smooth functions, they can be approximated by cubic splines with only a few parameters. Piecewise-constant, piecewise-linear or piecewise-quadratic functions could also be used, but these would typically require more parameters for the same quality of approximation. Note that the slight differences between the exact optimal inputs and the optimal inputs described by cubic splines often introduce only a

negligible difference in cost since small variations in sensitivity-seeking arcs typically have a much smaller impact on the cost than small variations in constraint-seeking arcs [157].

A cubic spline with π pieces and defined in an interval $\left[t^0, t^\pi\right]$ starts at the point (t^0, y^0), passes through the $\pi - 1$ intermediate points $(t^1, y^1), \ldots, (t^{\pi-1}, y^{\pi-1})$ and ends up at the point (t^π, y^π). This cubic spline is typically parameterized by the $\pi + 1$ coordinates $y^0, \ldots, y^\pi$ and 2 conditions at the endpoints t^0 and t^π (for example, on the second derivatives). Hence, $\pi + 3$ parameters are needed to describe the cubic spline.

In this chapter, to enable the computation of sensitivity-seeking input arcs described by cubic splines via forward integration of differential equations, a different interpretation is assigned to these $\pi + 3$ parameters. For the input u_j, these parameters are the following: three parameters correspond to the initial value $u_j(t^0)$, the initial first derivative $\dot{u}_j(t^0)$ and the initial second derivative $\ddot{u}_j(t^0)$, while the remaining π parameters $\mathbf{p}_j$ correspond to the third derivatives in the π intervals of the cubic spline. Hence, the input u_j can be described by the differential equation

$$u_j^{(3)}(t) = p_{j,1}, \quad t \in \left[t^0, t^1\right); \quad \ldots \quad ; u_j^{(3)}(t) = p_{j,\pi}, \quad t \in \left[t^{\pi-1}, t^\pi\right), \tag{8.27}$$

with the three initial values $u_j(t^0)$, $\dot{u}_j(t^0)$, and $\ddot{u}_j(t^0)$.

In the remainder, these $\pi + 3$ parameters will be considered as initial conditions for the sensitivity-seeking input arc. Note that the locations of the intermediate points are not input parameters since they are fixed at $t^m := (1 - w^m)\, t^0 + w^m t^\pi$ for all $m \in \{0, 1, \ldots, \pi\}$, where w^m is a constant that specifies the relative position of the intermediate point t^m with respect to t^0 and t^π, with $0 = w^0 < w^1 < \ldots < w^\pi = 1$.

8.4 Parsimonious Input Parameterization

8.4.1 Basic idea

The advantage of the approaches shown in the previous section is that they allow reducing the types of arcs that may appear in the optimal solution to a finite number, which results in a finite number of arc sequences if one assumes an upper bound on the number of arcs that are present in the optimal solution. Hence, instead of solving the original infinite-dimensional problem, one can simply perform numerical optimization for each arc sequence, using the switching times between arcs and the initial conditions of the arcs as decision variables. Then, one can either compare the optimal value of the cost function for that arc sequence to the optimal values provided by other sequences or check whether that arc sequence is optimal using the necessary conditions of optimality stated by the PMP (Pontryagin's maximum principle).

The generic idea of this approach, labeled *parsimonious input parameterization*, was first proposed by [157]. The updated version of this approach proposed here consists of the following steps:

1. Set the current optimal cost to infinity, generate a finite set of plausible arc sequences from all the input arcs that can occur, and choose an initial arc sequence.
2. Use a direct sequential approach to compute via numerical optimization (i) the optimal switching times to arcs of type 1, and (ii) the optimal switching times to and the initial conditions for arcs of type 3, which correspond to the optimal solution that uses the chosen arc sequence. At each iteration:
   (a) Integrate the states and inputs forward in time and store their time profiles.
   (b) Integrate the adjoint variables backward in time, using the stored states and inputs, and store their time profiles.
   (c) Compute the sensitivities with respect to the switching times and the initial conditions for the sensitivity-seeking arcs, using the stored states, inputs, and adjoint variables.
3. Check if the optimal cost for the chosen arc sequence is better than the current optimal cost and, if so, update the current optimal cost and arc sequence. Alternatively, check the necessary conditions of optimality for the solution returned by the optimization algorithm, using the states, inputs, adjoint variables, and Lagrange multipliers that were computed for that solution.
4. Choose a different arc sequence and repeat Steps 2-4 until all arc sequences are investigated.

The optimization in Step 2 typically uses algorithms that require the computation of gradients with respect to the decision variables at each iteration. The execution of this step is facilitated by the fact that the states can be computed via forward integration of the dynamic equations since the inputs can be generated simultaneously without knowledge of the value of the adjoint variables. Once the forward integration is complete, one can integrate backward in time to obtain the corresponding adjoint variables, which enables the computation of the gradients with respect to the decision variables and allows checking whether the necessary conditions of optimality are satisfied upon convergence of the optimization algorithm. The next subsections give more details about this implementation.

Remark 8.1. Note that, if the optimization in Step 2 can be solved to global optimality for each arc sequence, then the input trajectory with the best cost will be globally optimal. To enforce global optimality, one could approximate the terminal cost and constraints as explicit *polynomial* functions of the decision variables and compute the global solution to this polynomial optimization problem via reformulation as a semidefinite program [158]. Note that the fact of having fewer decision variables facilitates the whole procedure.

8.4.2 Dynamic model of an arc sequence

Let us consider a given arc sequence that includes $n_s + 1$ arcs of types 1 and 3, where n_s is the number of switching times to these arcs (one of these arcs starts at t_0, which is not counted as a switching time). These switching times $t_1, \ldots, t_{n_s}$ are considered as decision variables, while the switching times to arcs of type 2 are not decision variables since they depend on the states and cannot occur arbitrarily. We show next that, if one considers this

arc sequence and a set of rules that specify which inputs need to be adjusted when a pure-state path constraint becomes active, the inputs $\mathbf{u}(\cdot)$ are fully defined by the switching times $t_1, \ldots, t_{n_s}$, the final time t_f, and the initial conditions of the sensitivity-seeking arcs, which become the decision variables of the problem.

Note that, in addition to the switching times $t_1, \ldots, t_{n_s}$ considered as decision variables, other switchings between arcs occur when a pure-state path constraint $h_k\big(\mathbf{x}(t)\big) \leq 0$, for some $k = 1, \ldots, n_h$, becomes active. In that case, the inputs $\mathbf{u}(t)$ are simply adjusted such that this path constraint remains active and all the path constraints remain feasible. Note that it is always possible to adjust at least one input to make the new active path constraint remain active as guaranteed by Eq. (8.2b). The times at which a transition between arcs occur are called effective switching times in the remainder, and they include both the switching times considered as decision variables and the times at which a pure-state path constraint becomes active. However, the case of arc sequences with active pure-state path constraints is not detailed in this section, and it is described in Appendix G.2 instead.

Let us describe the inputs in the ith time interval $\big[t_{i-1}, t_i\big)$, for some $i = 1, \ldots, n_s + 1$, with $t_{n_s+1} = t_f$. For each input u_j, with $j = 1, \ldots, n_u$, there is a degree $\xi_{j,i} \geq 0$ for which a feedback law explicitly gives $u_j^{(\xi_{j,i})}(t)$ as a function of the states, the inputs, the time derivatives of the inputs, and the optional parameter vector $\mathbf{p}_{j,i}$ (that is, the constant third derivatives in the π_i pieces of the cubic spline if u_j is described by a cubic spline in this interval). This differential relationship requires specifying the initial conditions $u_j^{(\xi_{j,i}-1)}(t_{i-1}), \ldots, u_j(t_{i-1})$. The vector $\mathbf{p}_{j,i}$ is of dimension $b_{j,i}\pi_i$, where $b_{j,i}$ is a binary constant that specifies whether $\mathbf{p}_{j,i}$ exists or not, and each element $p_{j,i,m}$ is used only for $t \in \Big[t_i^{m-1}, t_i^m\Big)$, with the $\pi_i + 1$ time instants $t_i^0, t_i^1 \ldots, t_i^{\pi_i}$ specified by the constants $w_i^0, w_i^1 \ldots, w_i^{\pi_i}$. Then, the feedback law can be described as follows:

$$u_j^{(\xi_{j,i})}(t) = c_{j,i}\big(\mathbf{x}(t), \mathbf{p}_{j,i}, u_1^{(\xi_{1,i}-1)}(t), \ldots, u_1(t), \ldots, u_{n_u}^{(\xi_{n_u,i}-1)}(t), \ldots, u_{n_u}(t)\big), \tag{8.28}$$

with

$$\begin{aligned} \dot{u}_j^{(\xi_{j,i}-1)}(t) &= u_j^{(\xi_{j,i})}(t), \quad u_j^{(\xi_{j,i}-1)}(t_{i-1}) = u_{j,i}^{\xi_{j,i}-1}, \\ &\vdots \\ \dot{u}_j(t) &= u_j^{(1)}(t), \qquad\qquad u_j(t_{i-1}) = u_{j,i}^0. \end{aligned} \tag{8.29}$$

Note that it is possible to have $\xi_{j,i} = 0$, and, in this case, u_j is given by static feedback. However, if $\xi_{j,i} > 0$, the feedback is dynamic, and it is fully determined only if the initial conditions $u_{j,i}^{\xi_{j,i}-1}, \ldots, u_{j,i}^0$ are specified. Then, upon defining the $n_{z,i} := b_{1,i}\pi_i + \xi_{1,i} + \ldots +$

$b_{n_u,i}\pi_i + \xi_{n_u,i}$ states and initial conditions

$$\mathbf{z}_i(t) := \begin{bmatrix} \tilde{\mathbf{p}}_{1,i}(t) \\ \tilde{u}_{1,i}^{\xi_{1,i}-1}(t) \\ \vdots \\ \tilde{u}_{1,i}^{0}(t) \\ \vdots \\ \tilde{\mathbf{p}}_{n_u,i}(t) \\ \tilde{u}_{n_u,i}^{\xi_{n_u,i}-1}(t) \\ \vdots \\ \tilde{u}_{n_u,i}^{0}(t) \end{bmatrix}, \qquad \mathbf{z}_{i,0} := \begin{bmatrix} \mathbf{p}_{1,i} \\ u_{1,i}^{\xi_{1,i}-1} \\ \vdots \\ u_{1,i}^{0} \\ \vdots \\ \mathbf{p}_{n_u,i} \\ u_{n_u,i}^{\xi_{n_u,i}-1} \\ \vdots \\ u_{n_u,i}^{0} \end{bmatrix}, \tag{8.30}$$

one can describe their dynamics for $t \in \left[t_{i-1}, t_i\right)$ as

$$\dot{\mathbf{z}}_i(t) = \mathbf{q}_i\left(\mathbf{x}(t), \mathbf{z}_i(t)\right), \quad \mathbf{z}_i(t_{i-1}) = \mathbf{z}_{i,0}. \tag{8.31}$$

Then, it is possible to write that, for all $i = 1, \ldots, n_s + 1$, and for all $t \in \left[t_{i-1}, t_i\right)$,

$$\mathbf{q}_i\left(\mathbf{x}(t), \mathbf{z}_i(t)\right) = \begin{bmatrix} \mathbf{0}_{b_{1,i}\pi_i} \\ c_{1,i}\left(\mathbf{x}(t), \mathbf{z}_i(t)\right) \\ \vdots \\ \tilde{u}_{1,i}^{1}(t) \\ \vdots \\ \mathbf{0}_{b_{n_u,i}\pi_i} \\ c_{n_u,i}\left(\mathbf{x}(t), \mathbf{z}_i(t)\right) \\ \vdots \\ \tilde{u}_{n_u,i}^{1}(t) \end{bmatrix}, \tag{8.32}$$

and, for all $i = 1, \ldots, n_s + 1$, and for all $t \notin \left[t_{i-1}, t_i\right)$,

$$\mathbf{q}_i\left(\mathbf{x}(t), \mathbf{z}_i(t)\right) = \mathbf{0}_{n_{z,i}}. \tag{8.33}$$

Then, for the complete arc sequence, one defines the $n_z := n_x + n_{z,1} + \ldots + n_{z,n_s+1}$ extended states

$$\mathbf{z}(t) := \begin{bmatrix} \mathbf{x}(t) \\ \mathbf{z}_1(t) \\ \vdots \\ \mathbf{z}_{n_s+1}(t) \end{bmatrix} \tag{8.34}$$

and uses the control laws

$$\mathbf{u}(t) = \tilde{\mathbf{c}}\big(\mathbf{z}(t)\big), \tag{8.35}$$

where, for all $j = 1, \ldots, n_u$, for all $i = 1, \ldots, n_s + 1$, and for all $t \in \big[t_{i-1}, t_i\big)$,

$$\tilde{c}_j\big(\mathbf{z}(t)\big) = \begin{cases} \tilde{u}^0_{j,i}(t), & \text{if } \xi_{j,i} > 0 \\ c_{j,i}\big(\mathbf{x}(t), \mathbf{z}_i(t)\big), & \text{if } \xi_{j,i} = 0 \end{cases}, \tag{8.36}$$

which implies that the inputs $\mathbf{u}(t)$ are continuous for all $t \in \big[t_0, t_f\big]$ that is not an effective switching time. Moreover, the inputs that correspond to a particular arc sequence, given by the control laws $\tilde{\mathbf{c}}\big(\mathbf{z}(t)\big)$, can be fully characterized by a finite number of switching times $t_1, \ldots, t_{n_s}$ and initial conditions $\mathbf{z}_{1,0}, \ldots, \mathbf{z}_{n_s+1,0}$. Then, one can eliminate the input dependencies and rewrite the functions in Problem 8.1 in terms of $\mathbf{z}$, that is,

$$\tilde{\phi}\big(\mathbf{z}(t_f), t_f\big) := \phi\big(\mathbf{x}(t_f), t_f\big), \tag{8.37a}$$

$$\tilde{\boldsymbol{\omega}}\big(\mathbf{z}(t_f), t_f\big) := \boldsymbol{\omega}\big(\mathbf{x}(t_f), t_f\big), \tag{8.37b}$$

$$\tilde{\psi}\big(\mathbf{z}(t_f), t_f\big) := \psi\big(\mathbf{x}(t_f), t_f\big), \tag{8.37c}$$

$$\tilde{\mathbf{f}}\big(\mathbf{z}(t)\big) := \begin{bmatrix} \mathbf{f}\Big(\mathbf{x}(t), \tilde{\mathbf{c}}\big(\mathbf{z}(t)\big)\Big) \\ \mathbf{q}_1\big(\mathbf{x}(t), \mathbf{z}_1(t)\big) \\ \vdots \\ \mathbf{q}_{n_s+1}\big(\mathbf{x}(t), \mathbf{z}_{n_s+1}(t)\big) \end{bmatrix}, \tag{8.37d}$$

$$\tilde{\mathbf{g}}\big(\mathbf{z}(t)\big) := \mathbf{g}\Big(\mathbf{x}(t), \tilde{\mathbf{c}}\big(\mathbf{z}(t)\big)\Big), \tag{8.37e}$$

$$\tilde{\mathbf{h}}\big(\mathbf{z}(t)\big) := \mathbf{h}\big(\mathbf{x}(t)\big), \tag{8.37f}$$

$$\tilde{\mathbf{h}}^{(1)}\big(\mathbf{z}(t)\big) := \mathbf{h}^{(1)}\Big(\mathbf{x}(t), \tilde{\mathbf{c}}\big(\mathbf{z}(t)\big)\Big), \tag{8.37g}$$

with the initial conditions

$$\mathbf{z}_0 := \begin{bmatrix} \mathbf{x}_0 \\ \mathbf{z}_{1,0} \\ \vdots \\ \mathbf{z}_{n_s+1,0} \end{bmatrix}. \tag{8.38}$$

The system equations now read:

$$\dot{\mathbf{z}}(t) = \tilde{\mathbf{f}}\big(\mathbf{z}(t)\big), \quad \mathbf{z}(t_0) = \mathbf{z}_0. \tag{8.39}$$

8.4.3 Numerical optimization for a given arc sequence

To check whether a given arc sequence and the inputs that result from its feedback laws are the optimal solution to Problem (8.1), one uses the fact that any input trajectory $\mathbf{u}(\cdot)$ implementing that arc sequence is given by some switching times and initial conditions for the sensitivity-seeking arcs. Then, if the solutions $\mathbf{u}(\cdot)$ to Problem (8.1) are restricted to a particular arc sequence, the functionals $\mathscr{J}$, $\mathscr{O}$, and $\mathscr{T}$ reduce to the functions $\hat{\phi}$, $\hat{\boldsymbol{\omega}}$ and $\hat{\boldsymbol{\psi}}$ of the switching times $t_1,\ldots,t_{n_s}$, the final time t_f, and the initial conditions $\mathbf{z}_{1,0},\ldots,\mathbf{z}_{n_s+1,0}$, which is more convenient for numerical optimization. This numerical optimization problem corresponds to

$$\min_{t_1,\ldots,t_{n_s},t_f,\mathbf{z}_{1,0},\ldots,\mathbf{z}_{n_s+1,0}} \quad \hat{\phi}(t_1,\ldots,t_{n_s},t_f,\mathbf{z}_{1,0},\ldots,\mathbf{z}_{n_s+1,0}) = \tilde{\phi}\big(\mathbf{z}(t_f),t_f\big), \tag{8.40a}$$

$$\text{s.t.} \quad \hat{\boldsymbol{\omega}}(t_1,\ldots,t_{n_s},t_f,\mathbf{z}_{1,0},\ldots,\mathbf{z}_{n_s+1,0}) = \tilde{\boldsymbol{\omega}}\big(\mathbf{z}(t_f),t_f\big) = \mathbf{0}_{n_\omega}, \tag{8.40b}$$

$$\hat{\boldsymbol{\psi}}(t_1,\ldots,t_{n_s},t_f,\mathbf{z}_{1,0},\ldots,\mathbf{z}_{n_s+1,0}) = \tilde{\boldsymbol{\psi}}\big(\mathbf{z}(t_f),t_f\big) \leq \mathbf{0}_{n_\psi}, \tag{8.40c}$$

$$\dot{\mathbf{z}}(t) = \tilde{\mathbf{f}}\big(\mathbf{z}(t)\big), \quad \mathbf{z}(t_0) = \mathbf{z}_0, \tag{8.40d}$$

$$\tilde{\mathbf{g}}\big(\mathbf{z}(t)\big) \leq \mathbf{0}_{n_g}, \tag{8.40e}$$

$$\tilde{\mathbf{h}}\big(\mathbf{z}(t)\big) \leq \mathbf{0}_{n_h}. \tag{8.40f}$$

A direct sequential approach is used to find the switching times, final time, and initial conditions of the sensitivity-seeking arcs that are a solution to Problem (8.40), which is the restriction of Problem (8.1) to a particular arc sequence. Then, for any values of the decision variables $\boldsymbol{\tau} := \big(t_1,\ldots,t_{n_s},t_f,\mathbf{z}_{1,0},\ldots,\mathbf{z}_{n_s+1,0}\big)$, the terminal cost and constraints

$$\hat{\boldsymbol{\chi}}(\boldsymbol{\tau}) := \begin{bmatrix} \hat{\phi}(\boldsymbol{\tau}) \\ \hat{\boldsymbol{\omega}}(\boldsymbol{\tau}) \\ \hat{\boldsymbol{\psi}}(\boldsymbol{\tau}) \end{bmatrix} \tag{8.41}$$

can be computed via numerical integration of Eq. (8.39) and evaluation of the functions

$$\tilde{\boldsymbol{\chi}}\big(\mathbf{z}(t_f),t_f\big) := \begin{bmatrix} \tilde{\phi}\big(\mathbf{z}(t_f),t_f\big) \\ \tilde{\boldsymbol{\omega}}\big(\mathbf{z}(t_f),t_f\big) \\ \tilde{\boldsymbol{\psi}}\big(\mathbf{z}(t_f),t_f\big) \end{bmatrix}. \tag{8.42}$$

These values are passed to the numerical optimization algorithm with the purpose of computing the optimal values of $\boldsymbol{\tau}$. However, the gradients of $\hat{\boldsymbol{\chi}}$ with respect to the decision variables $\boldsymbol{\tau}$ also need to be supplied to the numerical optimization algorithm. These gradients can be computed via adjoint sensitivity analysis, which is efficient when the number of functions $\hat{\boldsymbol{\chi}}$ is small and facilitates checking the necessary conditions of optimality, as shown later. For this, each time Eq. (8.39) is integrated forward from t_0 to t_f to compute

the states $\mathbf{z}(t)$, the adjoint variables

$$\boldsymbol{\zeta}(t) := \begin{bmatrix} \boldsymbol{\lambda}(t) \\ \boldsymbol{\zeta}_1(t) \\ \vdots \\ \boldsymbol{\zeta}_{n_s+1}(t) \end{bmatrix} \tag{8.43}$$

that correspond to a single function $\tilde{\chi}$ are computed by integrating backward from t_f to t_0

$$\dot{\boldsymbol{\zeta}}(t) = -\frac{\partial \tilde{\mathbf{f}}}{\partial \mathbf{z}}\big(\mathbf{z}(t)\big)^{\mathrm{T}} \boldsymbol{\zeta}(t), \quad \boldsymbol{\zeta}(t_f) = \frac{\partial \tilde{\chi}}{\partial \mathbf{z}}\big(\mathbf{z}(t_f), t_f\big)^{\mathrm{T}}. \tag{8.44}$$

Furthermore, for each instant θ at which $\tilde{h}_k\big(\mathbf{z}(\theta^-)\big) < 0$ and $\tilde{h}_k\big(\mathbf{z}(\theta)\big) = 0$, for some $k = 1, \ldots, n_h$, which is equivalent to saying that $\tilde{h}_k\big(\mathbf{z}(t)\big) \leq 0$ becomes active at $t = \theta$ and that θ is an entry point, it holds that:

$$\boldsymbol{\zeta}(\theta^-) = \boldsymbol{\zeta}(\theta) - \frac{\partial \tilde{h}_k}{\partial \mathbf{z}}\big(\mathbf{z}(\theta^-)\big)^{\mathrm{T}} \frac{\Big[\tilde{\mathbf{f}}\big(\mathbf{z}(\theta^-)\big) - \tilde{\mathbf{f}}\big(\mathbf{z}(\theta)\big)\Big]^{\mathrm{T}} \boldsymbol{\zeta}(\theta)}{\tilde{h}_k^{(1)}\big(\mathbf{z}(\theta^-)\big)}. \tag{8.45}$$

Note that this integration requires the interpolation of the states $\mathbf{z}(t)$, whose values are known for a finite number of time points after the forward integration step.

The gradients of the functions $\hat{\boldsymbol{\chi}}$ with respect to the decision variables $\boldsymbol{\tau}$ are obtained from

$$\frac{\partial \hat{\chi}}{\partial t_i}(\boldsymbol{\tau})^{\mathrm{T}} = \sum_{m=1}^{\pi_i - 1} w_i^m \delta(t_i^m) + \delta(t_i) + \sum_{m=1}^{\pi_{i+1}-1} \left(1 - w_{i+1}^m\right) \delta(t_{i+1}^m), \quad \forall i = 1, \ldots, n_s, \tag{8.46}$$

$$\frac{\partial \hat{\chi}}{\partial t_f}(\boldsymbol{\tau})^{\mathrm{T}} = \sum_{m=1}^{\pi_{n_s+1}-1} w_{n_s+1}^m \delta(t_{n_s+1}^m) + \tilde{\mathbf{f}}\big(\mathbf{z}(t_f^-)\big)^{\mathrm{T}} \boldsymbol{\zeta}(t_f) + \frac{\partial \tilde{\chi}}{\partial t}\big(\mathbf{z}(t_f), t_f\big)^{\mathrm{T}}, \tag{8.47}$$

$$\frac{\partial \hat{\chi}}{\partial \mathbf{z}_{i,0}}(\boldsymbol{\tau})^{\mathrm{T}} = \boldsymbol{\zeta}_i(t_0), \quad \forall i = 1, \ldots, n_s + 1, \tag{8.48}$$

where $\delta(t) := \Big[\tilde{\mathbf{f}}\big(\mathbf{z}(t^-)\big) - \tilde{\mathbf{f}}\big(\mathbf{z}(t)\big)\Big]^{\mathrm{T}} \boldsymbol{\zeta}(t)$.

It would also be possible to compute higher-order derivatives of $\hat{\boldsymbol{\chi}}$ with respect to the decision variables, which would require the computation of derivatives of the states $\mathbf{z}(t)$ and adjoint variables $\boldsymbol{\zeta}(t)$ with respect to these decision variables. However, this computation is out of the scope of this chapter.

Another important aspect for successful numerical optimization is scaling. The values of the decision variables should be scaled, as well as the gradients with respect to these decision variables. The variables $t_1, \ldots, t_{n_s}$ are transformed to the new variables $\tilde{t}_1, \ldots, \tilde{t}_{n_s}$

and scaled with respect to their original interval $[t_0, t_f]$ to the interval $[0,1]$, whereas the variable t_f is transformed to $\tilde{t}_f$ and scaled with respect to its original interval $[t_0, t_{up}]$ to $[0,1]$, where t_{up} is the upper bound on the value of t_f. The conversion between original and scaled variables is given by the following equations:

$$\tilde{t}_i = \frac{t_i - t_0}{t_f - t_0} \Leftrightarrow t_i = t_0 + \left(t_f - t_0\right)\tilde{t}_i, \quad \forall i = 1,\ldots,n_s, \tag{8.49}$$

$$\tilde{t}_f = \frac{t_f - t_0}{t_{up} - t_0} \Leftrightarrow t_f = t_0 + \left(t_{up} - t_0\right)\tilde{t}_f, \tag{8.50}$$

which implies that the gradients of the functions $\hat{\boldsymbol{\chi}}$ with respect to the scaled decision variables are given by

$$\frac{\partial \hat{\chi}}{\partial \tilde{t}_i}(\boldsymbol{\tau})^{\mathrm{T}} = \left(t_f - t_0\right)\frac{\partial \hat{\chi}}{\partial t_i}(\boldsymbol{\tau})^{\mathrm{T}}, \quad \forall i = 1,\ldots,n_s, \tag{8.51}$$

$$\frac{\partial \hat{\chi}}{\partial \tilde{t}_f}(\boldsymbol{\tau})^{\mathrm{T}} = \left(t_{up} - t_0\right)\frac{\partial \hat{\chi}}{\partial t_f}(\boldsymbol{\tau})^{\mathrm{T}}. \tag{8.52}$$

8.4.4 Checking the PMP conditions

To check whether the solution specified by the optimal switching times and initial conditions of the sensitivity-seeking arcs for a particular arc sequence satisfies the necessary conditions of optimality given by the PMP, one defines the states

$$\bar{\mathbf{x}}(t) := \begin{bmatrix} \mathbf{x}(t) \\ \bar{\mathbf{x}}_1(t) \\ \vdots \\ \bar{\mathbf{x}}_{n_s+1}(t) \end{bmatrix} \tag{8.53}$$

and replaces the inputs $\mathbf{u}(t)$ by the control laws

$$\mathbf{u}(t) = \bar{\mathbf{u}}(t) + \tilde{\mathbf{c}}\big(\bar{\mathbf{x}}(t)\big), \tag{8.54}$$

where $\bar{\mathbf{u}}(t)$ is a vector of input perturbations. This implies that, if $\bar{\mathbf{u}}(t)$ is continuous for all $t \in \left[t_0, t_f\right]$ that is not an effective switching time, the same holds for $\mathbf{u}(t)$. Moreover, the inputs that correspond to a particular arc sequence can still be fully characterized by a finite number of switching times $t_1,\ldots,t_{n_s}$ and initial conditions $\mathbf{z}_{1,0},\ldots,\mathbf{z}_{n_s+1,0}$ since one can simply take $\bar{\mathbf{u}}(t) = \mathbf{0}_{n_u}$ in that case. Then, one can rewrite the problem functions and

the initial conditions as

$$\bar{\phi}\left(\bar{\mathbf{x}}(t_f), t_f\right) := \phi\left(\mathbf{x}(t_f), t_f\right), \tag{8.55a}$$
$$\bar{\boldsymbol{\omega}}\left(\bar{\mathbf{x}}(t_f), t_f\right) := \boldsymbol{\omega}\left(\mathbf{x}(t_f), t_f\right), \tag{8.55b}$$
$$\bar{\boldsymbol{\psi}}\left(\bar{\mathbf{x}}(t_f), t_f\right) := \boldsymbol{\psi}\left(\mathbf{x}(t_f), t_f\right), \tag{8.55c}$$
$$\bar{\mathbf{f}}\big(\bar{\mathbf{x}}(t), \bar{\mathbf{u}}(t)\big) := \begin{bmatrix} \mathbf{f}\Big(\mathbf{x}(t), \bar{\mathbf{u}}(t) + \tilde{\mathbf{c}}\big(\bar{\mathbf{x}}(t)\big)\Big) \\ \mathbf{q}_1\big(\mathbf{x}(t), \bar{\mathbf{x}}_1(t)\big) \\ \vdots \\ \mathbf{q}_{n_s+1}\big(\mathbf{x}(t), \bar{\mathbf{x}}_{n_s+1}(t)\big) \end{bmatrix}, \tag{8.55d}$$
$$\bar{\mathbf{g}}\big(\bar{\mathbf{x}}(t), \bar{\mathbf{u}}(t)\big) := \mathbf{g}\Big(\mathbf{x}(t), \bar{\mathbf{u}}(t) + \tilde{\mathbf{c}}\big(\bar{\mathbf{x}}(t)\big)\Big), \tag{8.55e}$$
$$\bar{\mathbf{h}}\big(\bar{\mathbf{x}}(t)\big) := \mathbf{h}\big(\mathbf{x}(t)\big), \tag{8.55f}$$
$$\bar{\mathbf{h}}^{(1)}\big(\bar{\mathbf{x}}(t), \bar{\mathbf{u}}(t)\big) := \mathbf{h}^{(1)}\Big(\mathbf{x}(t), \bar{\mathbf{u}}(t) + \tilde{\mathbf{c}}\big(\bar{\mathbf{x}}(t)\big)\Big), \tag{8.55g}$$
$$\bar{\mathbf{x}}_0 := \mathbf{z}_0. \tag{8.55h}$$

The system equations now read:

$$\dot{\bar{\mathbf{x}}}(t) = \bar{\mathbf{f}}\big(\bar{\mathbf{x}}(t), \bar{\mathbf{u}}(t)\big), \quad \bar{\mathbf{x}}(t_0) = \bar{\mathbf{x}}_0. \tag{8.56}$$

Hence, an equivalent reformulation of the original problem is constructed, which is used to check whether a solution with $\bar{\mathbf{u}}(t) = \mathbf{0}_{n_u}$ satisfies the necessary conditions of optimality. This reformulated problem reads

$$\min_{\bar{\mathbf{u}}(\cdot), t_1, \ldots, t_{n_s}, t_f, \mathbf{z}_{1,0}, \ldots, \mathbf{z}_{n_s+1,0}} \quad \hat{\mathscr{J}}(\bar{\mathbf{u}}(\cdot), \boldsymbol{\tau}) = \bar{\phi}\left(\bar{\mathbf{x}}(t_f), t_f\right), \tag{8.57a}$$
$$\text{s.t.} \quad \hat{\mathscr{O}}(\bar{\mathbf{u}}(\cdot), \boldsymbol{\tau}) = \bar{\boldsymbol{\omega}}\left(\bar{\mathbf{x}}(t_f), t_f\right) = \mathbf{0}_{n_\omega}, \tag{8.57b}$$
$$\hat{\mathscr{P}}(\bar{\mathbf{u}}(\cdot), \boldsymbol{\tau}) = \bar{\boldsymbol{\psi}}\left(\bar{\mathbf{x}}(t_f), t_f\right) \leq \mathbf{0}_{n_\psi}, \tag{8.57c}$$
$$\dot{\bar{\mathbf{x}}}(t) = \bar{\mathbf{f}}\big(\bar{\mathbf{x}}(t), \bar{\mathbf{u}}(t)\big), \quad \bar{\mathbf{x}}(t_0) = \bar{\mathbf{x}}_0, \tag{8.57d}$$
$$\bar{\mathbf{g}}\big(\bar{\mathbf{x}}(t), \bar{\mathbf{u}}(t)\big) \leq \mathbf{0}_{n_g}, \tag{8.57e}$$
$$\bar{\mathbf{h}}\big(\bar{\mathbf{x}}(t)\big) \leq \mathbf{0}_{n_h}. \tag{8.57f}$$

Upon convergence of the optimization algorithm to the optimal values of the decision variables $t_1^*, \ldots, t_{n_s}^*$, t_f^*, $\mathbf{z}_{1,0}^*, \ldots, \mathbf{z}_{n_s+1,0}^*$ for the particular arc sequence used in Problem (8.40), the necessary conditions of optimality for Problem (8.57) can finally be checked for $\bar{\mathbf{u}}(t) = \mathbf{0}_{n_u}$. These conditions are the following: if $(\bar{\mathbf{u}}^*(\cdot), t_1^*, \ldots, t_{n_s}^*, t_f^*, \mathbf{z}_{1,0}^*, \ldots, \mathbf{z}_{n_s+1,0}^*)$ is a solution to Problem (8.57) and $\bar{\mathbf{x}}^*(\cdot)$ is the corresponding n_z-dimensional trajectory of states, then there exist an n_z-dimensional trajectory of adjoint variables $\bar{\boldsymbol{\lambda}}^*(\cdot)$, an n_g-dimensional trajectory of Lagrange multipliers $\bar{\boldsymbol{\mu}}^*(\cdot)$, an n_h-dimensional trajectory of Lagrange multipliers $\bar{\boldsymbol{\eta}}^*(\cdot)$, an n_ω-dimensional vector of Lagrange multipliers $\bar{\boldsymbol{\xi}}^*$, and an n_ψ-dimensional

vector of Lagrange multipliers $\bar{\boldsymbol{\nu}}^*$ such that the conditions in Eqs. (G.10)–(G.34) in Appendix G.3 are satisfied. These conditions can be readily checked from the states, inputs, adjoint variables and Lagrange multipliers that are computed for the solution to Problem (8.40), as explained also in Appendix G.3.

8.5 Examples

In this section, the solution to specific dynamic optimization problems is shown. The first example corresponds to the maximization of the profit and the minimization of the batch time in an isothermal semi-batch reactor, the second corresponds to the maximization of the final amount of product in an isothermal semi-batch reactor, the third corresponds to the maximization of the amount of distillate in a batch distillation column subject to constraints on both the distillate and bottoms purities, and the fourth corresponds to the maximization of the final amount of product in a non-isothermal semi-batch reactor.

8.5.1 Maximization of profit and minimization of batch time in a chlorination reactor

The following example, which is a modified version of a case study presented in [19], corresponds to the chlorination of butanoic acid in the liquid phase[3] of an isothermal (at the temperature $T = 323$ K) homogeneous semi-batch reactor containing $S = 6$ species (chlorine or Cl_2, butanoic acid or BA, monochlorobutanoic acid or MBA, hydrochloric acid or HCl, dichlorobutanoic acid or DBA, and the solvent ethanol or Solv), whose numbers of moles $\mathbf{n}(t)$ are given by Eq. (8.13), which means that they can be written as linear functions of the extents $\mathbf{x}(t)$.

These $S = 6$ species are involved in the $R = 2$ reactions $\mathrm{R1 : BA + Cl_2 \rightarrow MBA + HCl}$ that produces the main product MBA, and $\mathrm{R2 : BA + 2Cl_2 \rightarrow DBA + 2HCl}$ that produces the side product DBA. Initially, the reactor contains 13 kmol of BA and 100 kmol of Solv. Then, the reactor is fed with $p = 1$ inlet, composed exclusively of Cl_2, with the flowrate $u_{in}(t)$ in kg s^{-1} subject to the bounds $u_{in,min} = 0$ and $u_{in,max} = 5$ kg s^{-1}. Hence, the structural matrices that characterize the system are the following:

$$\mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 1 & 0 & 0 \\ -2 & -1 & 0 & 2 & 1 & 0 \end{bmatrix}, \tag{8.58}$$

$$\mathbf{W}_{in} = \begin{bmatrix} 0.07100^{-1} & 0 & 0 & 0 & 0 & 0 \end{bmatrix}^{\mathrm{T}} \text{ mol kg}^{-1}, \tag{8.59}$$

$$\mathbf{n}_0 = \begin{bmatrix} 0 & 13000 & 0 & 0 & 0 & 100000 \end{bmatrix}^{\mathrm{T}} \text{ mol}. \tag{8.60}$$

[3] In practice, very high pressures would be needed to ensure that Cl_2 is in the liquid state. However, this fact has not been considered important in this context, due to the illustrative nature of this example.

Table 8.1 – Physical properties of the species in the reaction system of Problems (8.63) and (8.64).

Species	Cl_2	BA	MBA	HCl	DBA	Solv
m_w (kg mol^{-1})	0.07100	0.08812	0.12252	0.03645	0.15697	0.04600
ρ (kg L^{-1})	1.09300	0.85917	1.08553	1.48626	1.07000	0.79000

Table 8.2 – Numerical values used for Problems (8.63) and (8.64).

Variable	Value	Units
$k_{1,1}$	0.475783	L mol^{-1} s^{-1}
k_2	0.1	L mol^{-1}
o	10	\$ s^{-1}
c	1	\$ kg^{-1}
p_{MBA}	200	\$ mol^{-1}
m_{MBA}	1	-
n_{conv}	11.7	kmol
$n_{\mathrm{Cl_2},0}$	0	kmol
$n_{\mathrm{BA},0}$	13	kmol
$n_{\mathrm{Solv},0}$	100	kmol
$u_{in,min}$	0	kg s^{-1}
$u_{in,max}$	5	kg s^{-1}
V_{max}	10000	L

The reaction rates $r_{v,1}(t)$ and $r_{v,2}(t)$ are

$$r_{v,1}(t) = k_1 \frac{n_{\mathrm{BA}}(t) n_{\mathrm{Cl_2}}(t)}{V(t)}, \qquad k_1 = \frac{k_{1,1}}{0.4} \exp\left(5.34 - \tfrac{3760}{T[K]}\right), \tag{8.61a}$$

$$r_{v,2}(t) = k_2 \frac{n_{\mathrm{Cl_2}}(t)}{V(t)} r_{v,1}(t), \tag{8.61b}$$

with the rate constants $k_{1,1} = 0.475783$ L mol^{-1} s^{-1}, $k_2 = 0.1$ L mol^{-1}, and the volume

$$V(t) = \mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \mathbf{n}(t) = V_0 + \begin{bmatrix} V_{r,1} & V_{r,2} & V_{in} \end{bmatrix} \mathbf{x}(t), \tag{8.62}$$

where $V_{r,1} := \mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \mathbf{N}_1$, $V_{r,2} := \mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \mathbf{N}_2$, and $V_{in} := \mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \mathbf{W}_{in}$, from the S-dimensional diagonal matrices of densities $\boldsymbol{\rho}$ and of molecular weights $\mathbf{M}_w$, knowing that the species in this reaction system are characterized by the physical properties in Table 8.1.

Two different problems have been formulated for this reactor. All the numerical values used in these examples are summarized in Table 8.2. The first problem is the maximization of the profit of a single batch, taking into account the S-dimensional vector of prices of sale

$\mathbf{p} = \begin{bmatrix} 0 & 0 & 200 & 0 & 0 & 0 \end{bmatrix}^{\mathrm{T}}$ \$ mol^{-1}, the inlet cost $c = 1$ \$ kg^{-1} and the operating cost per unit of time $o = 10$ \$ s^{-1}. Hence, this problem is formulated as

$$\max_{\mathbf{u}(\cdot), t_f} \quad \mathscr{J}\left(\mathbf{u}(\cdot), t_f\right) = \mathbf{p}^{\mathrm{T}}\mathbf{n}(t_f) - c\, x_{in}(t_f) - o\, t_f, \tag{8.63a}$$

$$\text{s.t.} \quad \dot{\mathbf{x}}(t) = \mathbf{f}\big(\mathbf{x}(t), \mathbf{u}(t)\big) = \begin{bmatrix} \mathbf{r}_v(t) \\ u_{in}(t) \end{bmatrix}, \quad \mathbf{x}(t_0) = \mathbf{0}_{R+1}, \tag{8.63b}$$

$$\mathbf{g}\big(\mathbf{x}(t), \mathbf{u}(t)\big) = \begin{bmatrix} u_{in}(t) - u_{in,max} \\ u_{in,min} - u_{in}(t) \end{bmatrix} \leq \mathbf{0}_2. \tag{8.63c}$$

Figure 8.1 shows the input trajectories obtained for the optimal solution to Problem (8.63) with the parsimonious input parameterization and the analytical characterization of the sensitivity-seeking input arcs. The solution consists of 4 arcs: in the first arc, $u_{in}^*(t) = u_{in,max}$; in the second arc, $u_{in,min} < u_{in}^*(t) < u_{in,max}$; in the third arc, $u_{in}^*(t) = u_{in,max}$; in the fourth arc, $u_{in}^*(t) = u_{in,min}$. This results in an input trajectory described by the 3 input parameters t_1, t_2, t_3, which is equivalent to 4 decision variables since t_f is a free final time. The optimal switching times are $t_1^* = 14.2$ s, $t_2^* = 5918.4$ s, $t_3^* = 5982.1$ s, and the optimal final time is $t_f^* = 6258.4$ s. The optimal profit is 2.467×10^6 \$.

The second problem is the minimization of the batch time required for a weighted sum of the final numbers of moles, specified by the S-dimensional vector $\mathbf{m} = \begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix}^{\mathrm{T}}$, to reach the number of converted moles $n_{conv} = 0.9\, n_{\mathrm{BA},0} = 11.7$ kmol, subject to an upper bound on the volume $V_{max} = 10000$ L. Hence, this problem is formulated as

$$\min_{\mathbf{u}(\cdot), t_f} \quad \mathscr{J}\left(\mathbf{u}(\cdot), t_f\right) = \phi\left(\mathbf{x}(t_f), t_f\right) = t_f, \tag{8.64a}$$

$$\text{s.t.} \quad \mathscr{T}\left(\mathbf{u}(\cdot), t_f\right) = \psi\left(\mathbf{x}(t_f), t_f\right) = n_{conv} - \mathbf{m}^{\mathrm{T}}\mathbf{n}(t_f) \leq 0, \tag{8.64b}$$

$$\dot{\mathbf{x}}(t) = \mathbf{f}\big(\mathbf{x}(t), \mathbf{u}(t)\big) = \begin{bmatrix} \mathbf{r}_v(t) \\ u_{in}(t) \end{bmatrix}, \quad \mathbf{x}(t_0) = \mathbf{0}_{R+1}, \tag{8.64c}$$

$$\mathbf{g}\big(\mathbf{x}(t), \mathbf{u}(t)\big) = \begin{bmatrix} u_{in}(t) - u_{in,max} \\ u_{in,min} - u_{in}(t) \end{bmatrix} \leq \mathbf{0}_2, \tag{8.64d}$$

$$\mathbf{h}\big(\mathbf{x}(t)\big) = V(t) - V_{max} \leq 0. \tag{8.64e}$$

Figure 8.2 shows the input trajectories obtained for the optimal solution to Problem (8.64) with the parsimonious input parameterization and the analytical characterization of the sensitivity-seeking input arcs. The solution consists of 4 arcs: in the first arc, $u_{in}^*(t) = u_{in,max}$; in the second arc, $u_{in,min} < u_{in}^*(t) < u_{in,max}$; in the third arc, $u_{in}^*(t) = u_{in,max}$; in the fourth arc, $u_{in,min} < u_{in}^*(t) < u_{in,max}$ is adjusted to keep the path constraint $\bar{h}_1\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ active. This results in an input trajectory described by the 2 input parameters t_1, t_2, which is equivalent to 3 decision variables since t_f is a free final time. The optimal switching times are $t_1^* = 70.0$ s, $t_2^* = 899.0$ s, and the optimal final time is $t_f^* = 1306.15$ s. There is also an effective switching time $t_{3,1}^* = 1264.8$ s at the beginning of the fourth arc. The optimal

cost is $\bar{\phi}\left(\bar{\mathbf{x}}^*(t_f^*), t_f^*\right) = 1306.15$ s, the terminal constraint $\bar{\boldsymbol{\psi}}\left(\bar{\mathbf{x}}^*(t_f^*), t_f^*\right)$ is active, and the corresponding Lagrange multiplier is $\bar{\boldsymbol{\nu}}^* = 1.244$ s mol^{-1}. Hence, the necessary conditions of optimality in Eqs. (G.22)–(G.24) are satisfied.

Note that, despite the different cost functions and terminal constraints of these two problems, all the arcs of the optimal input $u_{in}^*(t)$ in both cases are either determined by the path constraints that are related to the input bounds and to the maximal volume or given by an optimal control law that can be determined according to the method described in Section 8.3. More specifically, this optimal control law is given by the following expression:

$$u_{in}^* = k_1 n_{\mathrm{Cl_2}} M_{w,\mathrm{Cl_2}} \frac{(V + 2k_2 n_{\mathrm{Cl_2}})(n_{\mathrm{BA}} + \frac{n_{\mathrm{Cl_2}}}{2}) + n_{\mathrm{BA}} n_{\mathrm{Cl_2}} V_{r,1} + \frac{k_2 n_{\mathrm{BA}} n_{\mathrm{Cl_2}}^2}{V} V_{r,2}}{V(V - V_{in} M_{w,\mathrm{Cl_2}} n_{\mathrm{Cl_2}})}. \tag{8.65}$$

In both cases, it is also possible to observe that the remaining necessary conditions of optimality are fully satisfied since $\bar{\mathscr{H}}\left(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t), \bar{\boldsymbol{\lambda}}^*(t), t_f^*, \bar{\mathbf{x}}^*(t_f^*), \bar{\boldsymbol{\xi}}^*, \bar{\boldsymbol{\nu}}^*\right)$ satisfies the condition in Eq. (G.20), $\frac{\partial \mathscr{L}}{\partial \bar{\mathbf{u}}}\left(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t), \bar{\boldsymbol{\lambda}}^*(t), \bar{\boldsymbol{\mu}}^*(t), \bar{\boldsymbol{\eta}}^*(t)\right)$ satisfies the condition in Eq. (G.26), and $\bar{\boldsymbol{\mu}}^*(t)$ and $\bar{\mathbf{g}}\left(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\right)$ (inferred from $\mathbf{u}^*(t)$) satisfy the conditions in Eqs. (G.27)–(G.29). Additionally, for the optimal solution to Problem (8.64), $\bar{\boldsymbol{\eta}}^*(t)$ and $\bar{\mathbf{h}}\left(\bar{\mathbf{x}}^*(t)\right)$ satisfy the conditions in Eqs. (G.30)–(G.34), and, at the only entry point θ (whose value $\bar{\boldsymbol{\pi}}^*(\theta)$ is indicated by a circle that coincides with the value of $\bar{\boldsymbol{\eta}}^*(\theta)$), the conditions in Eqs. (G.17)–(G.18) are also satisfied.

8.5.2 Maximization of the amount of product in an acetoacetylation reactor

The following example, which is a modified version of a case study presented in [132] for a reaction system studied by [114], describes the acetoacetylation of pyrrole in the liquid phase of an isothermal homogeneous semi-batch reactor with constant density. There are $S = 5$ species in the reactor (pyrrole or A, diketene or B, 2-acetoacetyl pyrrole or C, dehydroacetic acid or D, and oligomers or E), whose numbers of moles $\mathbf{n}(t)$ are given by Eq. (8.13), which means that they can be written as linear functions of the extents $\mathbf{x}(t)$.

These $S = 5$ species are involved in the $R = 3$ reactions R1 : A + B $\rightarrow$ C that produces the main product C, and R2 : 2B $\rightarrow$ D and R3 : B $\rightarrow$ E that produce the side products D and E. Initially, the reactor of volume $V_0 = 1$ L contains a mixture of A, B, C and D. Then, B is fed via $p = 1$ inlet with the concentration $c_{in,\mathrm{B}} = 5$ mol L^{-1} and the flowrate $u_{in}(t)$ in L min^{-1} subject to the bounds $u_{in,min} = 0$ and $u_{in,max} = 2 \times 10^{-3}$ L min^{-1}. Hence, the structural

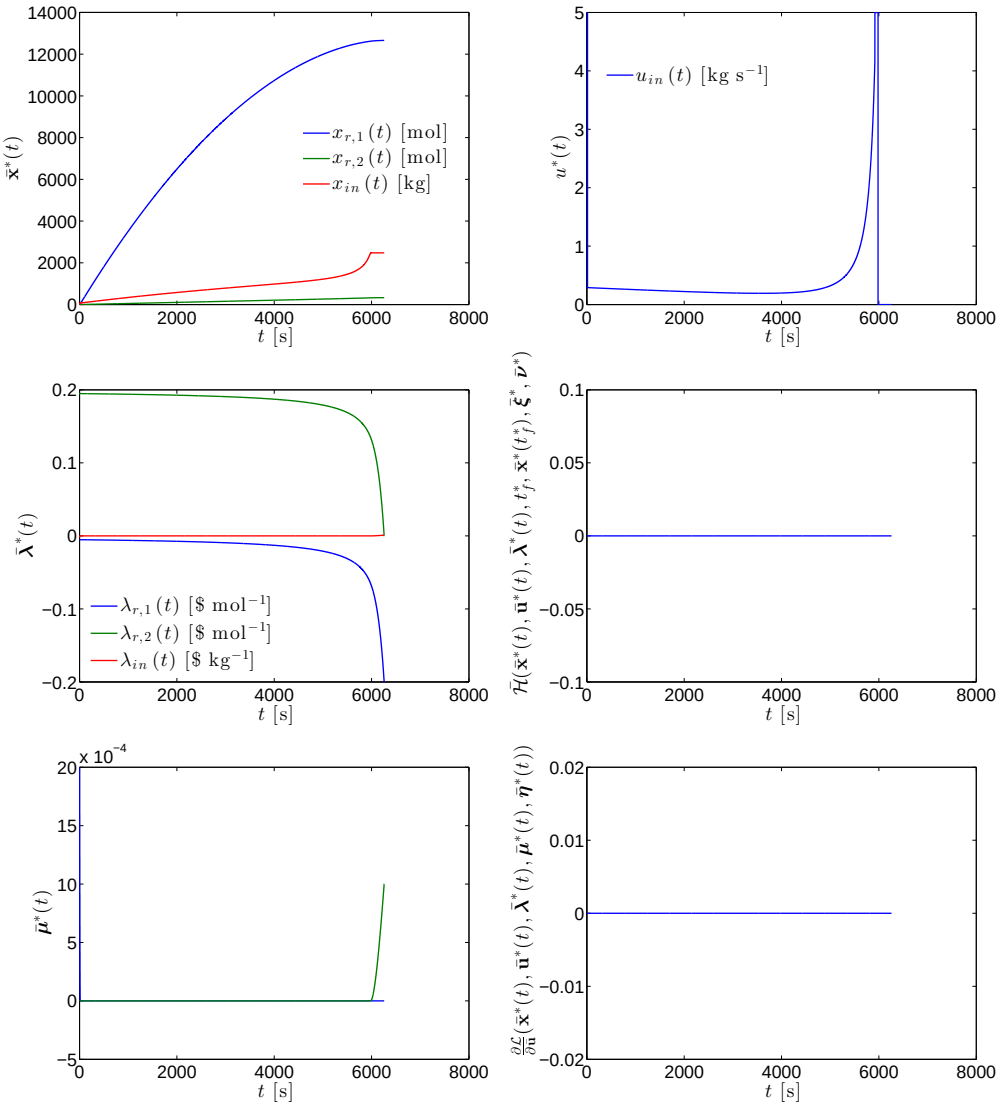

Figure 8.1 – Trajectories of the states, inputs, adjoint variables, Lagrange multipliers, reformulated Hamiltonian function and stationarity conditions for the optimal solution to Problem (8.63) with the parsimonious input parameterization and the analytical characterization of the sensitivity-seeking input arc.

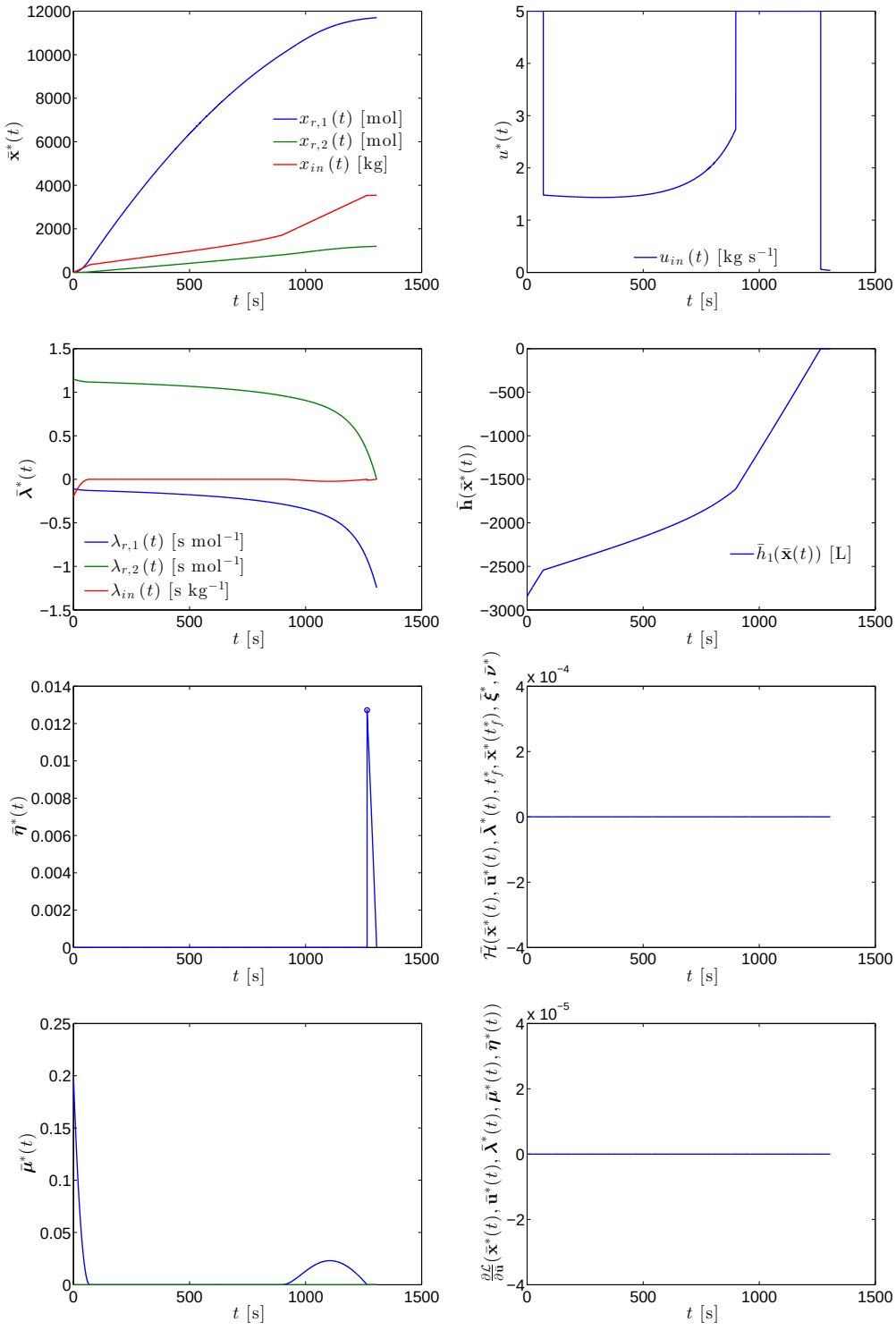

Figure 8.2 – Trajectories of the states, inputs, adjoint variables, Lagrange multipliers, reformulated Hamiltonian function and stationarity conditions for the optimal solution to Problem (8.64) with the parsimonious input parameterization and the analytical characterization of the sensitivity-seeking input arc.

Table 8.3 – Numerical values used for Problem (8.71).

Variable	Value	Units
k_1	0.053	L mol^{-1} min^{-1}
k_2	0.128	L mol^{-1} min^{-1}
k_3	0.028	min^{-1}
$c_{in,\mathrm{B}}$	5	mol L^{-1}
$n_{\mathrm{A},0}$	0.72	mol
$n_{\mathrm{B},0}$	0.05	mol
$n_{\mathrm{C},0}$	0.08	mol
$n_{\mathrm{D},0}$	0.01	mol
V_0	1	L
$c_{\mathrm{B},max}$	0.025	mol L^{-1}
$c_{\mathrm{D},max}$	0.15	mol L^{-1}
$t_{f,max}$	250	min
$u_{in,min}$	0	L min^{-1}
$u_{in,max}$	2×10^{-3}	L min^{-1}

matrices that characterize the system are the following:

$$\mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 0 & 0 \\ 0 & -2 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 & 1 \end{bmatrix}, \tag{8.66}$$

$$\mathbf{W}_{in} = \begin{bmatrix} 0 & 5 & 0 & 0 & 0 \end{bmatrix}^{\mathrm{T}} \text{ mol L}^{-1}, \tag{8.67}$$

$$\mathbf{n}_0 = \begin{bmatrix} 0.72 & 0.05 & 0.08 & 0.01 & 0 \end{bmatrix}^{\mathrm{T}} \text{ mol}. \tag{8.68}$$

The reaction rates $r_{v,1}(t)$, $r_{v,2}(t)$ and $r_{v,3}(t)$ are

$$r_{v,1}(t) = k_1 \frac{n_{\mathrm{A}}(t) n_{\mathrm{B}}(t)}{V(t)}, \tag{8.69a}$$

$$r_{v,2}(t) = k_2 \frac{n_{\mathrm{B}}^2(t)}{V(t)}, \tag{8.69b}$$

$$r_{v,3}(t) = k_3 n_{\mathrm{B}}(t), \tag{8.69c}$$

with the rate constants $k_1 = 0.053$ L mol^{-1} min^{-1}, $k_2 = 0.128$ L mol^{-1} min^{-1}, and $k_3 = 0.028$ min^{-1}, and the volume

$$V(t) = V_0 + x_{in}(t). \tag{8.70}$$

The problem consists in maximizing the final amount of product C in less than $t_{f,max} = 250$ min, subject to upper bounds on the final concentrations of B and D, namely $c_{\mathrm{B},max} =$

0.025 mol L^{-1} and $c_{D,max} = 0.15$ mol L^{-1}. All the numerical values used in this example are summarized in Table 8.3. Hence, this problem is formulated as

$$\max_{\mathbf{u}(\cdot),t_f} \quad \mathscr{J}\left(\mathbf{u}(\cdot),t_f\right) = n_C(t_f), \tag{8.71a}$$

$$\text{s.t.} \quad \mathscr{T}\left(\mathbf{u}(\cdot),t_f\right) = \boldsymbol{\psi}\left(\mathbf{x}(t_f),t_f\right) = \begin{bmatrix} n_B(t_f) - c_{B,max}V(t_f) \\ n_D(t_f) - c_{D,max}V(t_f) \\ t_f - t_{f,max} \end{bmatrix} \leq \mathbf{0}_3, \tag{8.71b}$$

$$\dot{\mathbf{x}}(t) = \mathbf{f}\big(\mathbf{x}(t),\mathbf{u}(t)\big) = \begin{bmatrix} \mathbf{r}_v(t) \\ u_{in}(t) \end{bmatrix}, \quad \mathbf{x}(t_0) = \mathbf{0}_{R+1}, \tag{8.71c}$$

$$\mathbf{g}\big(\mathbf{x}(t),\mathbf{u}(t)\big) = \begin{bmatrix} u_{in}(t) - u_{in,max} \\ u_{in,min} - u_{in}(t) \end{bmatrix} \leq \mathbf{0}_2. \tag{8.71d}$$

Figure 8.3 shows the input trajectories obtained for the optimal solution to Problem (8.71) with the parsimonious input parameterization and the analytical characterization of the sensitivity-seeking input arcs. The solution consists of 3 arcs: in the first arc, $u_{in}^*(t) = u_{in,max}$; in the second arc, $u_{in,min} < u_{in}^*(t) < u_{in,max}$; in the third arc, $u_{in}^*(t) = u_{in,min}$. This results in an input trajectory described by the 3 input parameters t_1, t_2, $u_{1,2}^0$, which is equivalent to 4 decision variables since t_f is a free final time. The optimal switching times are $t_1^* = 5.57$ min, $t_2^* = 230.01$ min, and the optimal final time is $t_f^* = 250$ min. The optimal initial condition of the dynamic feedback of the second arc, which corresponds to the initial value of $u_{in}^*(t)$ in this arc, is $u_{1,2}^{0*} = 1.299 \times 10^{-3}$ L min^{-1}. The optimal cost is $n_C^*(t_f^*) = 0.5137$ mol, all the terminal constraints $\bar{\boldsymbol{\psi}}^*\left(\bar{\mathbf{x}}^*(t_f^*),t_f^*\right)$ are active, and the corresponding Lagrange multipliers are $\bar{\boldsymbol{\nu}}^* = \begin{bmatrix} 0.1816 & 0.7625 & 5.7 \times 10^{-4} \end{bmatrix}$. Hence, the necessary conditions of optimality in Eqs. (G.22)–(G.24) are satisfied.

Again, all the arcs of the optimal input $u_{in}^*(t)$ are either determined by the path constraints that are related to the input bounds or given by an optimal control law that can be determined according to the method described in Section 8.3. In this case, since the number of reactions is $R = 3$, the optimal value of $u_{in}^*(t)$ results from dynamic feedback. More specifically, this optimal control law is given by the following expression:

$$\begin{aligned} \dot{u}_{in}^* = & \frac{2c_{in,B}V(8k_2^2n_B^4 + 4c_{in,B}^2u_{in}^2V^2 - c_{in,B}n_Bu_{in}V(5u_{in}+7k_3V))}{2c_{in,B}n_BV^2(-n_B+c_{in,B}V)} \\ & + \frac{2c_{in,B}V(2k_2n_B^2(4n_Bu_{in}+5k_3n_BV-6c_{in,B}u_{in}V)+n_B^2(u_{in}^2+5k_3u_{in}V+3k_3^2V^2))}{2c_{in,B}n_BV^2(-n_B+c_{in,B}V)} \\ & + \frac{k_1^2n_An_B^2(-2n_An_B+n_B^2+6c_{in,B}n_AV-2c_{in,B}n_BV)}{2c_{in,B}n_BV^2(-n_B+c_{in,B}V)} \\ & - \frac{2k_1n_An_B(2k_2n_B^2(n_B-5c_{in,B}V)+V(k_3n_B(n_B-6c_{in,B}V)+c_{in,B}u_{in}(-5n_B+7c_{in,B}V)))}{2c_{in,B}n_BV^2(-n_B+c_{in,B}V)}. \end{aligned} \tag{8.72}$$

It is also possible to observe that the remaining necessary conditions of optimality are fully satisfied since $\bar{\mathscr{H}}\left(\bar{\mathbf{x}}^*(t),\bar{\mathbf{u}}^*(t),\bar{\boldsymbol{\lambda}}^*(t),t_f^*,\bar{\mathbf{x}}^*(t_f^*),\bar{\boldsymbol{\xi}}^*,\bar{\boldsymbol{\nu}}^*\right)$ satisfies the condition in Eq. (G.20), $\frac{\partial \mathscr{L}}{\partial \bar{\mathbf{u}}}\left(\bar{\mathbf{x}}^*(t),\bar{\mathbf{u}}^*(t),\bar{\boldsymbol{\lambda}}^*(t),\bar{\boldsymbol{\mu}}^*(t),\bar{\boldsymbol{\eta}}^*(t)\right)$ satisfies the condition in Eq. (G.26), and

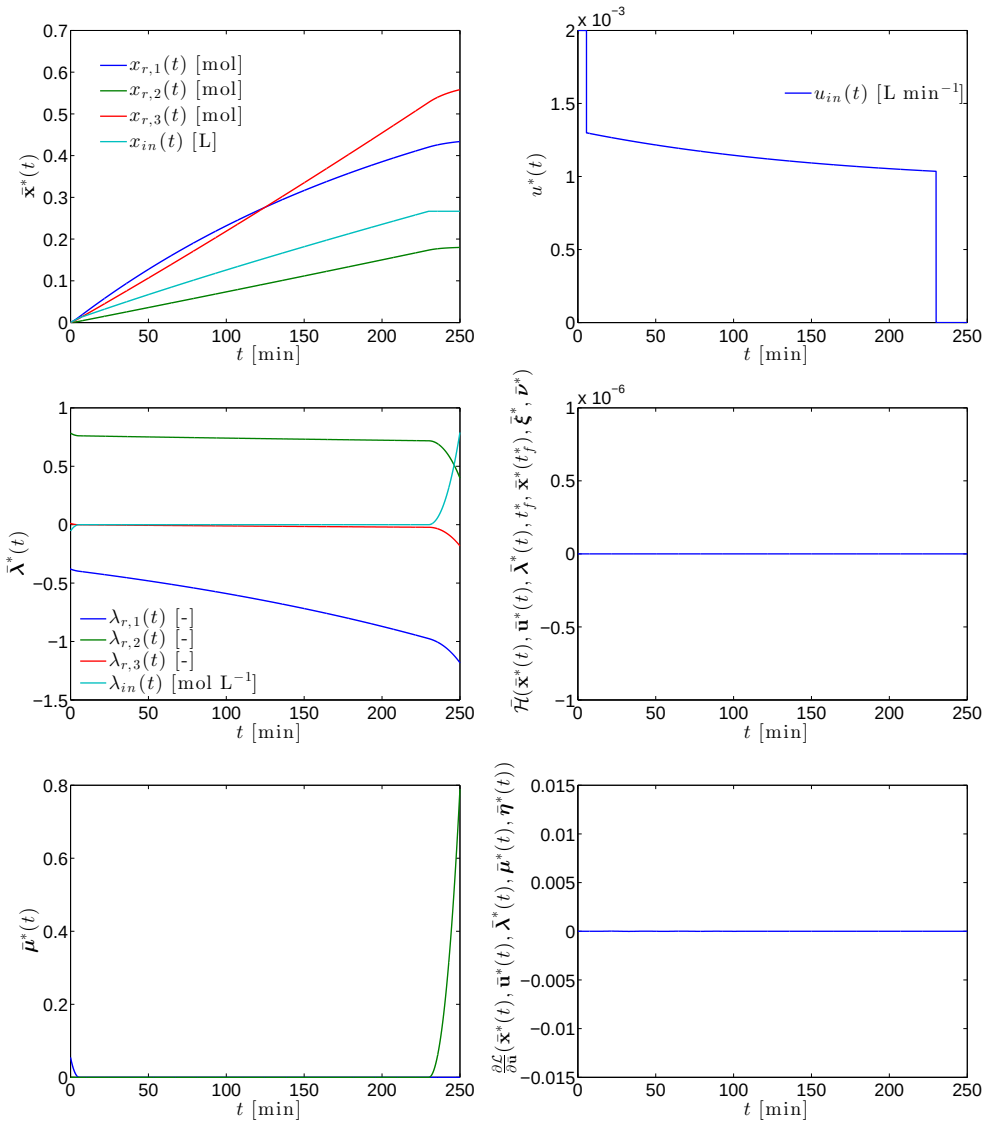

Figure 8.3 – Trajectories of the states, inputs, adjoint variables, Lagrange multipliers, reformulated Hamiltonian function and stationarity conditions for the optimal solution to Problem (8.71) with the parsimonious input parameterization and the analytical characterization of the sensitivity-seeking input arc.

$\bar{\boldsymbol{\mu}}^*(t)$ and $\bar{\mathbf{g}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big)$ (inferred from $\mathbf{u}^*(t)$) satisfy the conditions in Eqs. (G.27)–(G.29).

Since the sensitivity-seeking optimal control law is relatively complicated, it is worth using a more practical approach to parameterize the sensitivity-seeking arc, namely its description using cubic splines. Figure 8.4 shows the input trajectories obtained for the optimal solution to Problem (8.71) with the parsimonious input parameterization and the description of the sensitivity-seeking input arc using cubic splines. The solution consists of 3 arcs: in the first arc, $u_{in}^*(t) = u_{in,max}$; in the second arc, $u_{in,min} < u_{in}^*(t) < u_{in,max}$, and a cubic spline with $\pi = 1$ piece and no intermediate points is used; in the third arc, $u_{in}^*(t) = u_{in,min}$. This results in an input trajectory described by the 6 input parameters t_1, t_2, $u_{1,2}^0$, $u_{1,2}^1$, $u_{1,2}^2$, $p_{1,2}$, which is equivalent to 7 decision variables since t_f is a free final time. The optimal switching times are $t_1^* = 5.61$ min, $t_2^* = 229.99$ min, and the optimal final time is $t_f^* = 250$ min. The optimal initial conditions for the second arc include the initial value, initial derivative, initial second derivative, and the constant third derivative of the cubic spline (with $\pi_2 = 1$ piece) that describes $u_{in}^*(t)$ in this arc: $u_{1,2}^{0*} = 1.294 \times 10^{-3}$ L min^{-1}, $u_{1,2}^{1*} = -1.88 \times 10^{-6}$ L min^{-2}, $u_{1,2}^{2*} = 6.6 \times 10^{-9}$ L min^{-3}, $p_{1,2}^* = 0.7 \times 10^{-12}$ L min^{-4}. The optimal cost is $n_{\mathrm{C}}^*(t_f^*) = 0.5137$ mol, all the terminal constraints $\bar{\boldsymbol{\psi}}^*\big(\bar{\mathbf{x}}^*(t_f^*), t_f^*\big)$ are active, and the corresponding Lagrange multipliers are $\bar{\boldsymbol{\nu}}^* = \begin{bmatrix} 0.1816 & 0.7625 & 5.7 \times 10^{-4} \end{bmatrix}$. Hence, the necessary conditions of optimality in Eqs. (G.22)–(G.24) are satisfied.

It is interesting to note that the parameterization of the sensitivity-seeking arcs using cubic splines also satisfies the necessary conditions of optimality, and this parameterization also results in inputs and a cost that are virtually indistinguishable from the optimal inputs and optimal cost obtained with the analytical characterization of the sensitivity-seeking arcs.

Finally, it is also possible to compare the input trajectories obtained with both (i) the parsimonious parameterization and the description of the sensitivity-seeking input arc using cubic splines and (ii) the piecewise-constant parameterization of a direct method implemented using ACADO, a toolkit for dynamic optimization [155]. Figure 8.5 shows these input trajectories and the cost as a function of the number of input parameters. The parsimonious parameterization outperforms the piecewise-constant parameterization using the same number of parameters (6 parameters), which results in a rather coarse input trajectory and provides a worse cost, that is, $n_{\mathrm{C}}^*(t_f^*) = 0.5103$ mol; about 50 parameters are needed for the piecewise-constant parameterization to obtain an equally smooth input trajectory with a similar cost.

8.5.3 Maximization of the amount of distillate in a batch distillation column

The following example is the reformulation of the problem proposed in [159] for a binary batch distillation column, where the objective is the maximization of the amount of distillate, subject to constraints on the molar fraction of the component B in the distillate (at least $x_{\mathrm{B},D,min} = 0.8$) and bottoms (at most $x_{\mathrm{B},B,max} = 0.2$), in less than $t_{f,max} = 3$ h. The

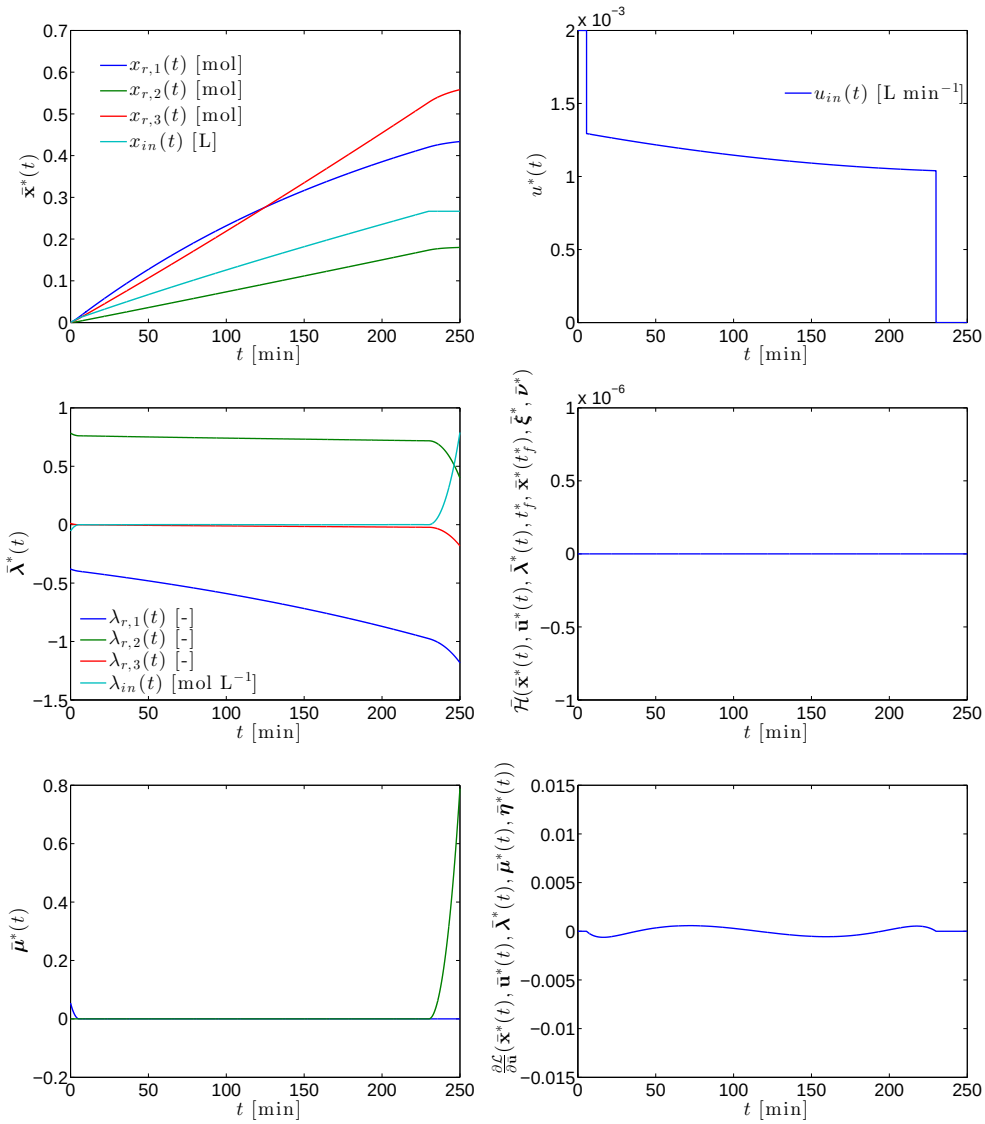

Figure 8.4 – Trajectories of the states, inputs, adjoint variables, Lagrange multipliers, reformulated Hamiltonian function and stationarity conditions for the optimal solution to Problem (8.71) with the parsimonious input parameterization and the description of the sensitivity-seeking input arc using cubic splines.

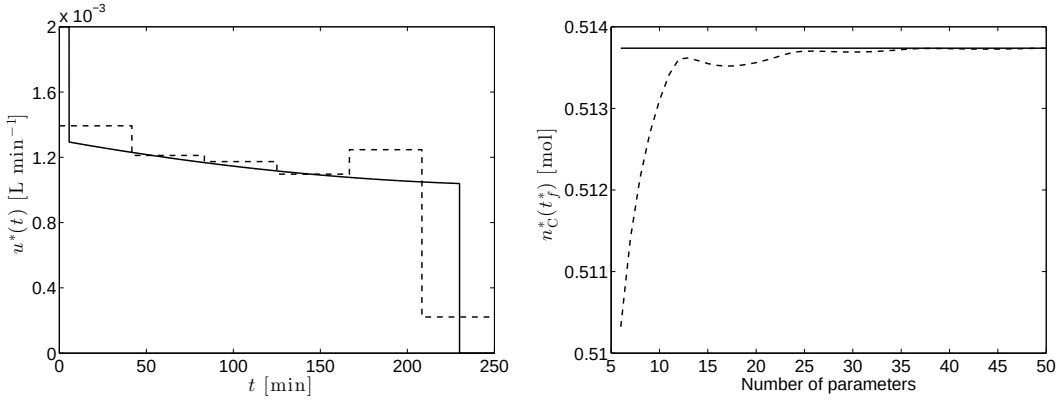

Figure 8.5 – Input trajectories (left) and cost (right) for the optimal solution to Problem (8.71). Solid lines represent the parsimonious parameterization using 6 parameters, and dashed lines represent the piecewise-constant parameterization of a direct method.

problem can be formulated mathematically using numbers of moles as states as follows:

$$\max_{r(t)} \quad D(t_f) \tag{8.73a}$$

$$\text{s.t.} \quad n_{\mathrm{B},D}(t_f) \geq x_{\mathrm{B},D,min} D(t_f), \tag{8.73b}$$

$$n_{\mathrm{B},B}(t_f) \leq x_{\mathrm{B},B,max} B(t_f), \tag{8.73c}$$

$$t_f \leq t_{f,max}, \tag{8.73d}$$

$$\dot{D} = V(1-r), \qquad D(0) = 0, \tag{8.73e}$$

$$\dot{B} = V(r-1), \qquad B(0) = B_0, \tag{8.73f}$$

$$\dot{n}_{\mathrm{B},B} = V(-y_{\mathrm{B},B}) + Vr x_{\mathrm{B},1}, \qquad n_{\mathrm{B},B}(0) = x_{\mathrm{B},0} B_0, \tag{8.73g}$$

$$\dot{n}_{\mathrm{B},1} = V(y_{\mathrm{B},B} - y_{\mathrm{B},1}) + Vr(x_{\mathrm{B},2} - x_{\mathrm{B},1}), \quad n_{\mathrm{B},1}(0) = x_{\mathrm{B},0} M, \tag{8.73h}$$

$$\dot{n}_{\mathrm{B},2} = V(y_{\mathrm{B},1} - y_{\mathrm{B},2}) + Vr(x_{\mathrm{B},3} - x_{\mathrm{B},2}), \quad n_{\mathrm{B},2}(0) = x_{\mathrm{B},0} M, \tag{8.73i}$$

$$\dot{n}_{\mathrm{B},3} = V(y_{\mathrm{B},2} - y_{\mathrm{B},3}) + Vr(y_{\mathrm{B},3} - x_{\mathrm{B},3}), \quad n_{\mathrm{B},3}(0) = x_{\mathrm{B},0} M, \tag{8.73j}$$

$$\dot{n}_{\mathrm{B},D} = V(1-r) y_{\mathrm{B},3}, \qquad n_{\mathrm{B},D}(0) = 0, \tag{8.73k}$$

$$0 \leq r(t) \leq 1, \tag{8.73l}$$

with $x_{\mathrm{B},B} := \frac{n_{\mathrm{B},B}}{B}$, $x_{\mathrm{B},n} := \frac{n_{\mathrm{B},n}}{M}$ for $n = 1,2,3$, and $y_{\mathrm{B},n} = \frac{\alpha x_{\mathrm{B},n}}{1+(\alpha-1)x_{\mathrm{B},n}}$ for $n = B,1,2,3$. In this model, B and D are the molar amounts in the bottoms and in the distillate tank, $n_{\mathrm{B},B}$, $n_{\mathrm{B},n}$ and $n_{\mathrm{B},D}$ are the number of moles of B in the bottoms, the liquid phase of the nth tray and the distillate tank, $x_{\mathrm{B},B}$ and $y_{\mathrm{B},B}$ are the molar fractions of B in the liquid phase and in the vapor of the bottoms, $x_{\mathrm{B},n}$ and $y_{\mathrm{B},n}$ are the molar fractions of B in the liquid phase and in the vapor of the nth tray, $V = 50$ kmol h^{-1} is the vapor flow rate in the column, $\alpha = 2.25$ is the relative volatility, $B_0 = 115$ kmol is the initial charge in the bottoms, $x_{\mathrm{B},0} = 0.4$ is the molar fraction of B in the initial charge, $M = 5$ kmol is the liquid holdup on each tray, and $r := \frac{L}{V}$ is the internal reflux ratio, with L the liquid flow rate in the column. All the

Table 8.4 – Numerical values used for Problem (8.76).

Variable	Value	Units
V	50	kmol h^{-1}
α	2.25	-
B_0	115	kmol
$x_{B,0}$	0.4	-
M	5	kmol
$x_{B,D,min}$	0.8	-
$x_{B,B,max}$	0.2	-
$t_{f,max}$	3	h

numerical values used in this example are summarized in Table 8.4.

Reduced-order model. Note that the 7 states in Problem (8.73) can be reduced to only 5 states, by using the state transformation

$$D(t) = M_{T,D}(t), \tag{8.74a}$$
$$B(t) = B_0 - M_{T,D}(t), \tag{8.74b}$$
$$n_{B,B}(t) = x_{B,0}B_0 - M_{B,1}(t), \tag{8.74c}$$
$$n_{B,1}(t) = x_{B,0}M + M_{B,1}(t) - M_{B,2}(t), \tag{8.74d}$$
$$n_{B,2}(t) = x_{B,0}M + M_{B,2}(t) - M_{B,3}(t), \tag{8.74e}$$
$$n_{B,3}(t) = x_{B,0}M + M_{B,3}(t) - M_{B,D}(t), \tag{8.74f}$$
$$n_{B,D}(t) = M_{B,D}(t), \tag{8.74g}$$

where $M_{T,D}(t)$ is the net number of moles of all species that has transferred from tray 3 to the distillate tank, and $M_{B,1}(t)$, $M_{B,2}(t)$, $M_{B,3}(t)$, $M_{B,D}(t)$ are the net numbers of moles of B that have transferred from the bottoms to tray 1, from tray 1 to tray 2, from tray 2 to tray 3, and from tray 3 to the distillate tank, respectively. These new states $\mathbf{x}(t)$ are described by the differential equations

$$\dot{M}_{T,D} = V(1-r), \qquad M_{T,D}(0) = 0, \tag{8.75a}$$
$$\dot{M}_{B,1} = V(y_{B,B} - r x_{B,1}), \quad M_{B,1}(0) = 0, \tag{8.75b}$$
$$\dot{M}_{B,2} = V(y_{B,1} - r x_{B,2}), \quad M_{B,2}(0) = 0, \tag{8.75c}$$
$$\dot{M}_{B,3} = V(y_{B,2} - r x_{B,3}), \quad M_{B,3}(0) = 0, \tag{8.75d}$$
$$\dot{M}_{B,D} = V(1-r)y_{B,3}, \qquad M_{B,D}(0) = 0. \tag{8.75e}$$

With this reduced-order model, the optimization problem can be written as

$$\max_{\mathbf{u}(\cdot),t_f} \quad \mathscr{J}\left(\mathbf{u}(\cdot),t_f\right) = D(t_f), \tag{8.76a}$$

$$\text{s.t.} \quad \mathscr{T}\left(\mathbf{u}(\cdot),t_f\right) = \boldsymbol{\psi}\left(\mathbf{x}(t_f),t_f\right) = \begin{bmatrix} x_{\mathrm{B},D,min}D(t_f) - n_{\mathrm{B},D}(t_f) \\ n_{\mathrm{B},B}(t_f) - x_{\mathrm{B},B,max}B(t_f) \\ t_f - t_{f,max} \end{bmatrix} \leq \mathbf{0}_3, \tag{8.76b}$$

$$\dot{\mathbf{x}}(t) = \mathbf{f}\big(\mathbf{x}(t),\mathbf{u}(t)\big) = \begin{bmatrix} V\left(1-r(t)\right) \\ V\left(\frac{\alpha n_{\mathrm{B},B}(t)/B(t)}{1+(\alpha-1)n_{\mathrm{B},B}(t)/B(t)} - r(t)n_{\mathrm{B},1}(t)/M\right) \\ V\left(\frac{\alpha n_{\mathrm{B},1}(t)/M}{1+(\alpha-1)n_{\mathrm{B},1}(t)/M} - r(t)n_{\mathrm{B},2}(t)/M\right) \\ V\left(\frac{\alpha n_{\mathrm{B},2}(t)/M}{1+(\alpha-1)n_{\mathrm{B},2}(t)/M} - r(t)n_{\mathrm{B},3}(t)/M\right) \\ V\left(1-r(t)\right)\frac{\alpha n_{\mathrm{B},3}(t)/M}{1+(\alpha-1)n_{\mathrm{B},3}(t)/M} \end{bmatrix},$$

$$\mathbf{x}(t_0) = \mathbf{0}_5, \tag{8.76c}$$

$$\mathbf{g}\big(\mathbf{x}(t),\mathbf{u}(t)\big) = \begin{bmatrix} r(t)-1 \\ -r(t) \end{bmatrix} \leq \mathbf{0}_2. \tag{8.76d}$$

Even with these 5 states, the analytical approach to parameterize sensitivity-seeking arcs would yield very complex results. In fact, the analytical parameterization would already be quite complex if a similar problem were solved for a batch distillation columm with 2 trays instead of 3 trays. Then, for this problem, cubic splines are very useful to parameterize the sensitivity-seeking arcs.

Figure 8.6 shows the input trajectories obtained for the optimal solution to Problem (8.76) with the parsimonious input parameterization and the description of the sensitivity-seeking input arcs using cubic splines. The solution consists of 3 arcs: in the first arc, $r^*(t) = 1$; in the second arc, $0 < r^*(t) < 1$, and a cubic spline with $\pi = 2$ pieces and an intermediate point specified by $w^1 = 0.875$ is used; in the third arc, $r^*(t) = 0$. This results in an input trajectory described by the 7 input parameters t_1, t_2, $u^0_{1,2}$, $u^1_{1,2}$, $u^2_{1,2}$, $p_{1,2,1}$, $p_{1,2,2}$, which is equivalent to 8 decision variables since t_f is a free final time. The optimal switching times are $t_1^* = 0.3595$ h, $t_2^* = 2.8834$ h, and the optimal final time is $t_f^* = 3$ h. The optimal initial conditions for the second arc include the initial value, initial derivative, initial second derivative, and the constant third derivative in the $\pi_2 = 2$ pieces of the cubic spline that describes $r^*(t)$ in this arc: $u^{0*}_{1,2} = 0.6711$, $u^{1*}_{1,2} = 0.0406\,\mathrm{h}^{-1}$, $u^{2*}_{1,2} = -0.0052\,\mathrm{h}^{-2}$, $p^*_{1,2,1} = 0.0036\,\mathrm{h}^{-3}$, $p^*_{1,2,2} = 46.1526\,\mathrm{h}^{-3}$. The optimal cost is $D^*(t_f^*) = 40.3228$ kmol, all the terminal constraints $\bar{\boldsymbol{\psi}}^*\left(\bar{\mathbf{x}}^*(t_f^*),t_f^*\right)$ are active, and the corresponding Lagrange multipliers are $\bar{\boldsymbol{\nu}}^* = \begin{bmatrix} 5.3073 & 0.1722 & 7.9199 \end{bmatrix}$. Hence, the necessary conditions of optimality in Eqs. (G.22)–(G.24) are satisfied.

It is also possible to observe that the remaining necessary conditions of optimality are almost fully satisfied since not only $\bar{\mathscr{H}}\left(\bar{\mathbf{x}}^*(t),\bar{\mathbf{u}}^*(t),\bar{\boldsymbol{\lambda}}^*(t),t_f^*,\bar{\mathbf{x}}^*(t_f^*),\bar{\boldsymbol{\xi}}^*,\bar{\boldsymbol{\nu}}^*\right)$ but also

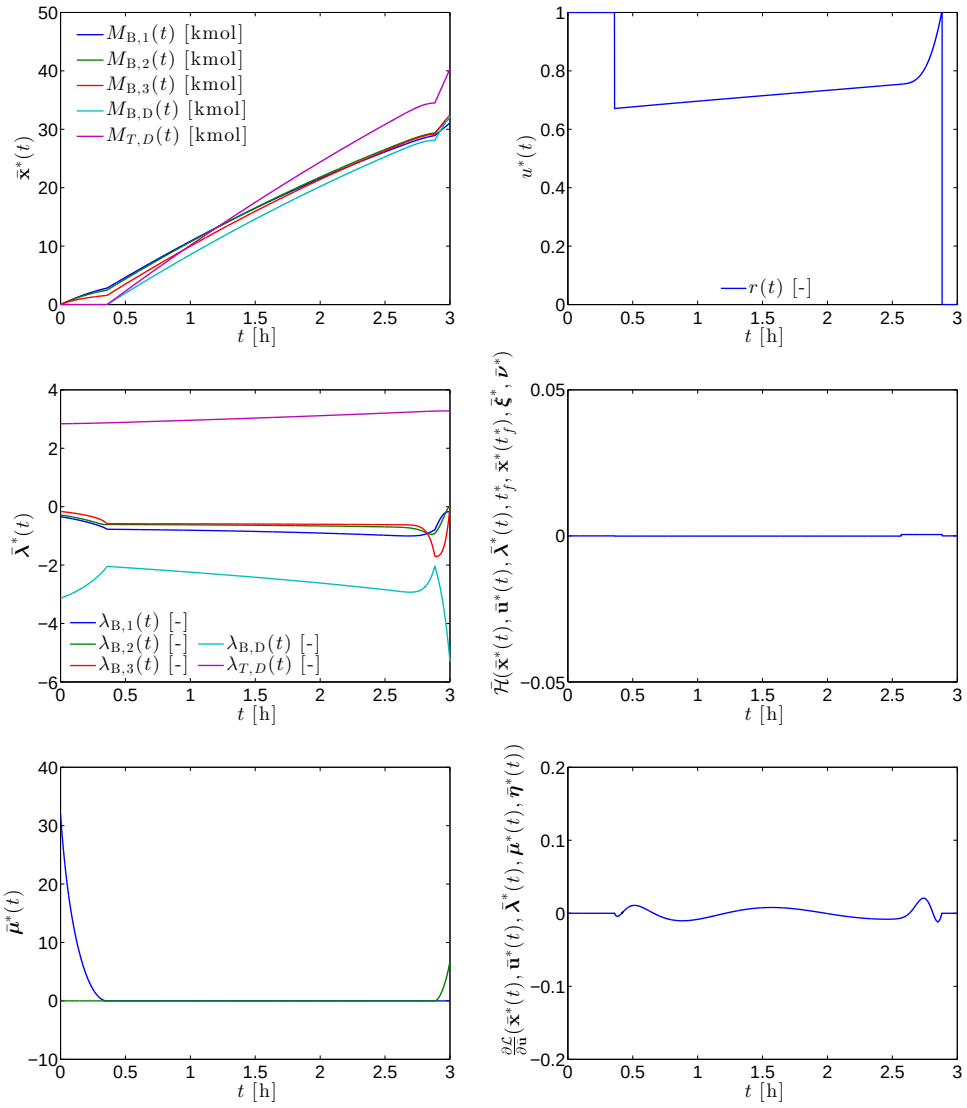

Figure 8.6 – Trajectories of the states, inputs, adjoint variables, Lagrange multipliers, reformulated Hamiltonian function and stationarity conditions for the optimal solution to Problem (8.76) with the parsimonious input parameterization and the description of the sensitivity-seeking input arc using cubic splines.

$\frac{\partial \mathscr{L}}{\partial \bar{\mathbf{u}}}\left(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t), \bar{\boldsymbol{\lambda}}^*(t), \bar{\boldsymbol{\mu}}^*(t), \bar{\boldsymbol{\eta}}^*(t)\right)$ satisfy the conditions in Eqs. (G.20) and (G.26) in an approximate way, and $\bar{\boldsymbol{\mu}}^*(t)$ and $\bar{\mathbf{g}}\left(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\right)$ (inferred from $\mathbf{u}^*(t)$) satisfy the conditions in Eqs. (G.27)–(G.29).

It is interesting to note in this case that $\bar{\mathscr{H}}\left(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t), \bar{\boldsymbol{\lambda}}^*(t), t_f^*, \bar{\mathbf{x}}^*(t_f^*), \bar{\boldsymbol{\xi}}^*, \bar{\boldsymbol{\nu}}^*\right)$ and $\frac{\partial \mathscr{L}}{\partial \bar{\mathbf{u}}}\left(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t), \bar{\boldsymbol{\lambda}}^*(t), \bar{\boldsymbol{\mu}}^*(t), \bar{\boldsymbol{\eta}}^*(t)\right)$ are only approximately equal to zero, due to the parameterization of the sensitivity-seeking arc using cubic splines. However, this slight deviation from the necessary conditions of optimality is of reduced practical importance since the exact optimal inputs and the corresponding optimal cost would be virtually indistinguishable from the inputs and cost obtained with this parsimonious parameterization.

8.5.4 Maximization of the amount of product in a non-isothermal semi-batch reactor

The following example is an adaptation of a dynamic optimization problem that was originally presented in [157], which corresponds to a non-isothermal reaction in a homogeneous semi-batch reactor. The same reference also proposed a locally optimal solution with 3 arcs, although subsequent references showed that two other local solutions with 5 arcs and better cost exist [160, 159]. However, only the solution with the best known cost, known as analytical solution 3 in [160], will be investigated here. The semi-batch reactor in this example contains $S = 4$ species (A, B, C, or D), whose numbers of moles $\mathbf{n}(t)$ and heat $Q(t)$ are given by Eq. (8.13), which means that they can be written as linear functions of the extents $\mathbf{x}(t)$.

These $S = 4$ species are involved in the $R = 2$ reactions R1 : A + B → C that produces the main product C, and R2 : C → D that produces the side product D. Initially, the reactor of volume $V_0 = 1$ L contains 10 mol of A and 1.1685 kmol of B at the temperature $T_0 = 323$ K. Then, B is fed via $p = 1$ inlet with the concentration $c_{in,\mathrm{B}} = 20$ mol L^{-1} and the flowrate $u_{in}(t)$ in L h^{-1} subject to the bounds $u_{in,min} = 0$ and $u_{in,max} = 1$ L h^{-1}. Furthermore, the reactor exchanges the heat power $q_{ex}(t)$ in MJ h^{-1} subject to the bounds $q_{ex,min} = -3$ MJ h^{-1} and $q_{ex,max} = 1$ MJ h^{-1}, the inlet does not contribute to the heat balance since its temperature is equal to the reference temperature $T_{ref} = 273$ K, the reaction mixture is characterized by the constant volumetric heat capacity $\rho c_p = 1.5 \times 10^{-3}$ MJ L^{-1} K^{-1} and the reaction enthalpies are $\Delta H_{r,1} = -0.030$ MJ mol^{-1} and $\Delta H_{r,2} = -0.010$ MJ mol^{-1}. Note that, in contrast to the previous references that considered the same example, the temperature $T(t)$ is not considered here as an input, but rather as a variable that can be computed from the states, not only for consistency with the previous parts of this chapter, but also because this corresponds to the more realistic situation where the temperature is not piecewise-continuous but rather piecewise-continuously differentiable. Instead of the temperature, another variable will be considered as an input, namely the exchanged heat power $q_{ex}(t)$, which can typically be assumed to be piecewise-continuous. Hence, the

structural matrices that characterize the system are the following:

$$\mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 0 \\ 0 & 0 & -1 & 1 \end{bmatrix}, \qquad \Delta\mathbf{H}_r = \begin{bmatrix} -0.030 \\ -0.010 \end{bmatrix} \text{ MJ mol}^{-1}, \tag{8.77}$$

$$\mathbf{W}_{in} = \begin{bmatrix} 0 & 20 & 0 & 0 \end{bmatrix}^{\mathrm{T}} \text{ mol L}^{-1}, \qquad \check{\mathbf{T}}_{in} = 0 \text{ MJ L}^{-1}, \tag{8.78}$$

$$\mathbf{n}_0 = \begin{bmatrix} 10 & 1.1685 & 0 & 0 \end{bmatrix}^{\mathrm{T}} \text{ mol}, \qquad Q_0 = V_0 \rho c_p \left(T_0 - T_{ref} \right). \tag{8.79}$$

The reaction rates $r_{v,1}(t)$ and $r_{v,2}(t)$ are

$$r_{v,1}(t) = k_1(t) \frac{n_{\mathrm{A}}(t) n_{\mathrm{B}}(t)}{V(t)}, \quad k_1(t) = k_{1,0} \exp\left(-\frac{E_{a,1}}{RT(t)} \right), \tag{8.80a}$$

$$r_{v,2}(t) = k_2(t) n_{\mathrm{C}}(t), \qquad k_2(t) = k_{2,0} \exp\left(-\frac{E_{a,2}}{RT(t)} \right), \tag{8.80b}$$

with the rate constants $k_{1,0} = 4 \text{ L mol}^{-1} \text{ h}^{-1}$, $k_{2,0} = 800 \text{ h}^{-1}$, the activation temperatures $\frac{E_{a,1}}{R} = \frac{6000}{8.31}$ K and $\frac{E_{a,2}}{R} = \frac{20000}{8.31}$ K, the volume

$$V(t) = V_0 + x_{in}(t), \tag{8.81}$$

and the temperature

$$T(t) = \frac{Q(t)}{V(t) \rho c_p} + T_{ref}. \tag{8.82}$$

The problem consists in maximizing the final amount of product C in this non-isothermal reactor in less than $t_{f,max} = 0.5$ h, subject to an upper bound on the volume $V_{max} = 1.1$ L, lower and upper bounds on the temperature $T_{min} = 293$ K and $T_{max} = 323$ K, and an upper bound on the heat power produced by the reactions $q_{rx,max} = 0.15 \text{ MJ h}^{-1}$. All the numerical values used in this example are summarized in Table 8.5. Note that, in contrast to the previous examples, there are multiple inputs, namely $\mathbf{u}(t) = \begin{bmatrix} u_{in}(t) & q_{ex}(t) \end{bmatrix}^{\mathrm{T}}$. Hence,

Table 8.5 – Numerical values used for Problem (8.83).

Variable	Value	Units
$k_{1,0}$	4	L mol^{-1} h^{-1}
$k_{2,0}$	800	h^{-1}
$E_{a,1}/R$	6000/8.31	K
$E_{a,2}/R$	20000/8.31	K
$\Delta H_{r,1}$	-0.030	MJ mol^{-1}
$\Delta H_{r,2}$	-0.010	MJ mol^{-1}
$c_{in,\text{B}}$	20	mol L^{-1}
ρc_p	1.5 $\times 10^{-3}$	MJ L^{-1} K^{-1}
T_{ref}	273	K
$n_{\text{A},0}$	10	mol
$n_{\text{B},0}$	1.1685	mol
$n_{\text{C},0}$	0	mol
V_0	1	L
T_0	323	K
$t_{f,max}$	0.5	h
$u_{in,min}$	0	L h^{-1}
$u_{in,max}$	1	L h^{-1}
$q_{ex,min}$	-3	MJ h^{-1}
$q_{ex,max}$	1	MJ h^{-1}
V_{max}	1.1	L
T_{min}	293	K
T_{max}	323	K
$q_{rx,max}$	0.15	MJ h^{-1}

this problem is formulated as

$$\max_{\mathbf{u}(\cdot),t_f} \quad \mathscr{J}\big(\mathbf{u}(\cdot),t_f\big) = n_{\mathrm{C}}(t_f), \tag{8.83a}$$

$$\text{s.t.} \quad \mathscr{T}\big(\mathbf{u}(\cdot),t_f\big) = \boldsymbol{\psi}\big(\mathbf{x}(t_f),t_f\big) = t_f - t_{f,max} \leq 0, \tag{8.83b}$$

$$\dot{\mathbf{x}}(t) = \mathbf{f}\big(\mathbf{x}(t),\mathbf{u}(t)\big) = \begin{bmatrix} \mathbf{r}_v(t) \\ u_{in}(t) \\ q_{ex}(t) \end{bmatrix}, \quad \mathbf{x}(t_0) = \mathbf{0}_{R+2}, \tag{8.83c}$$

$$\mathbf{g}\big(\mathbf{x}(t),\mathbf{u}(t)\big) = \begin{bmatrix} u_{in}(t) - u_{in,max} \\ u_{in,min} - u_{in}(t) \\ q_{ex}(t) - q_{ex,max} \\ q_{ex,min} - q_{ex}(t) \end{bmatrix} \leq \mathbf{0}_4, \tag{8.83d}$$

$$\mathbf{h}\big(\mathbf{x}(t)\big) = \begin{bmatrix} V(t) - V_{max} \\ T(t) - T_{max} \\ T_{min} - T(t) \\ -\Delta\mathbf{H}_r^{\mathrm{T}}\mathbf{r}_v(t) - q_{rx,max} \end{bmatrix} \leq \mathbf{0}_4. \tag{8.83e}$$

Figure 8.7 shows the input trajectories obtained for the optimal solution to Problem (8.83) with the parsimonious input parameterization and the description of the sensitivity-seeking input arcs using cubic splines. The solution consists of 5 arcs: in the first arc, since the path constraint $\bar{h}_4\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ becomes active immediately, $u_{in}^*(t) = u_{in,max}$, and $q_{ex,min} < q_{ex}^*(t) < q_{ex,max}$ is adjusted to keep the path constraint $\bar{h}_4\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ active; in the second arc, $u_{in,min} < u_{in}^*(t) < u_{in,max}$ is adjusted to keep the path constraint $\bar{h}_4\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ active, and $q_{ex,min} < q_{ex}^*(t) < q_{ex,max}$ is adjusted to keep the path constraint $\bar{h}_3\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ active; in the third arc, $u_{in}^*(t) = u_{in,min}$ to keep the path constraint $\bar{h}_1\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ active, and $q_{ex,min} < q_{ex}^*(t) < q_{ex,max}$ is adjusted to keep the path constraint $\bar{h}_4\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ active; in the fourth arc, $u_{in}^*(t) = u_{in,min}$ to keep the path constraint $\bar{h}_1\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ active, and $q_{ex,min} < q_{ex}^*(t) < q_{ex,max}$ is adjusted to keep the path constraint $\bar{h}_2\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ active; in the fifth arc, $u_{in}^*(t) = u_{in,min}$ to keep the path constraint $\bar{h}_1\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ active, and $q_{ex,min} < q_{ex}^*(t) < q_{ex,max}$, and a cubic spline with $\pi = 1$ piece and no intermediate points is used. This results in an input trajectory described by the 5 input parameters t_1, $u_{2,2}^0$, $u_{2,2}^1$, $u_{2,2}^2$, $p_{2,2}$, which is equivalent to 6 decision variables since t_f is a free final time. The single optimal switching time is $t_1^* = 0.3828$ h, and the optimal final time is $t_f^* = 0.5$ h. The optimal initial conditions for the fifth arc include the initial value, initial derivative, initial second derivative, and the constant third derivative of the cubic spline (with $\pi_2 = 1$ piece) that describes $q_{ex}^*(t)$ in this arc: $u_{2,2}^{0*} = -0.2858$ MJ h^{-1}, $u_{2,2}^{1*} = 1.0477$ MJ h^{-2}, $u_{2,2}^{2*} = 0.0654$ MJ h^{-3}, $p_{2,2}^* = 0.0023$ MJ h^{-4}. There are also 4 effective switching times $t_{1,1}^* \approx 0$ h, $t_{1,2}^* = 0.0233$ h, $t_{1,3}^* = 0.2701$ h, $t_{1,4}^* = 0.3445$ h at the beginning of the first, second, third, and fourth arcs. The optimal cost is $n_{\mathrm{C}}^*(t_f^*) = 2.0529$ mol, the terminal constraint $\bar{\boldsymbol{\psi}}\big(\bar{\mathbf{x}}^*(t_f^*),t_f^*\big)$ is active, and the corresponding Lagrange multiplier is $\bar{\boldsymbol{\nu}}^* = 1.8225$ mol s^{-1}. Hence, the necessary conditions of optimality in Eqs. (G.22)–(G.24) are satisfied.

As in the previous problems, all the arcs of the optimal inputs $u_{in}^*(t)$ and $q_{ex}^*(t)$ are either determined by the path constraints that are related to the input bounds and to the maximal volume, the minimal and maximal temperatures, and the maximal heat power produced by the reactions, or given by an optimal control law that can be determined according to the method described in Section 8.3. Let us analyze the situation for each arc.

In the first and third arcs, the optimal input $q_{ex}^*(t)$ is determined by the pure-state path constraint $\bar{h}_4\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ such that it remains active. In this case, the optimal control law is given by the expression:

$$\begin{aligned} q_{ex}^* = {} & \Delta \mathbf{H}_r^{\mathrm{T}} \mathbf{r}_v \\ & + \rho c_p \left(u_{in}^* \left(T - T_{ref} \right) - T u_{in}^* \frac{\Delta H_{r,1} k_1 n_{\mathrm{A}} \left(c_{in,\mathrm{B}} V - n_{\mathrm{B}} \right)}{\Delta H_{r,1} k_1 n_{\mathrm{A}} n_{\mathrm{B}} \frac{E_{a,1}}{RT} + \Delta H_{r,2} k_2 n_{\mathrm{C}} V \frac{E_{a,2}}{RT}} \right. \\ & \left. + T \frac{\Delta H_{r,1} k_1^2 n_{\mathrm{A}} n_{\mathrm{B}} \left(n_{\mathrm{A}} + n_{\mathrm{B}} \right) + \Delta H_{r,2} k_2 V \left(k_2 n_{\mathrm{C}} V - k_1 n_{\mathrm{A}} n_{\mathrm{B}} \right)}{\Delta H_{r,1} k_1 n_{\mathrm{A}} n_{\mathrm{B}} \frac{E_{a,1}}{RT} + \Delta H_{r,2} k_2 n_{\mathrm{C}} V \frac{E_{a,2}}{RT}} \right). \end{aligned} \tag{8.84}$$

In the second and fourth arcs, the optimal input $q_{ex}^*(t)$ is determined by the pure-state path constraints $\bar{h}_3\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ and $\bar{h}_2\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ such that they remain active. In both cases, the optimal control law is given by the expression:

$$q_{ex}^* = \Delta \mathbf{H}_r^{\mathrm{T}} \mathbf{r}_v + \rho c_p u_{in}^* \left(T - T_{ref} \right). \tag{8.85}$$

In the second arc, the optimal input $u_{in}^*(t)$ is determined by the pure-state path constraint $\bar{h}_4\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ such that it remains active, while $\bar{h}_3\big(\bar{\mathbf{x}}^*(t)\big) \leq 0$ is also active. In this case, the optimal control law is given by the expression:

$$u_{in}^* = \frac{\Delta H_{r,1} k_1^2 n_{\mathrm{A}} n_{\mathrm{B}} \left(n_{\mathrm{A}} + n_{\mathrm{B}} \right) + \Delta H_{r,2} k_2 V \left(k_2 n_{\mathrm{C}} V - k_1 n_{\mathrm{A}} n_{\mathrm{B}} \right)}{\Delta H_{r,1} k_1 n_{\mathrm{A}} \left(c_{in,\mathrm{B}} V - n_{\mathrm{B}} \right)}. \tag{8.86}$$

In the fifth arc, the optimal input $q_{ex}^*(t)$ is sensitivity-seeking, and the input arc is described using a cubic spline. However, since this reaction system is relatively simple, it would also be possible to use an analytical characterization of this sensitivity-seeking input arc. Then, the 4 input parameters needed to describe the cubic spline would not be necessary, and the input trajectory would be described by only 1 input parameter, the switching time t_1, or 2 decision variables if the free final time t_f is also considered. In that case, the optimal control law would be given by the expression:

$$q_{ex}^* = \Delta \mathbf{H}_r^{\mathrm{T}} \mathbf{r}_v + \rho c_p \left(u_{in}^* \left(T - T_{ref} \right) - T u_{in}^* \frac{c_{in,\mathrm{B}} V - n_{\mathrm{B}}}{n_{\mathrm{B}} \left(\frac{E_{a,1}}{RT} - \frac{E_{a,2}}{RT} \right)} - T \frac{k_1 n_{\mathrm{A}} n_{\mathrm{B}}}{n_{\mathrm{C}} \frac{E_{a,2}}{RT}} \right). \tag{8.87}$$

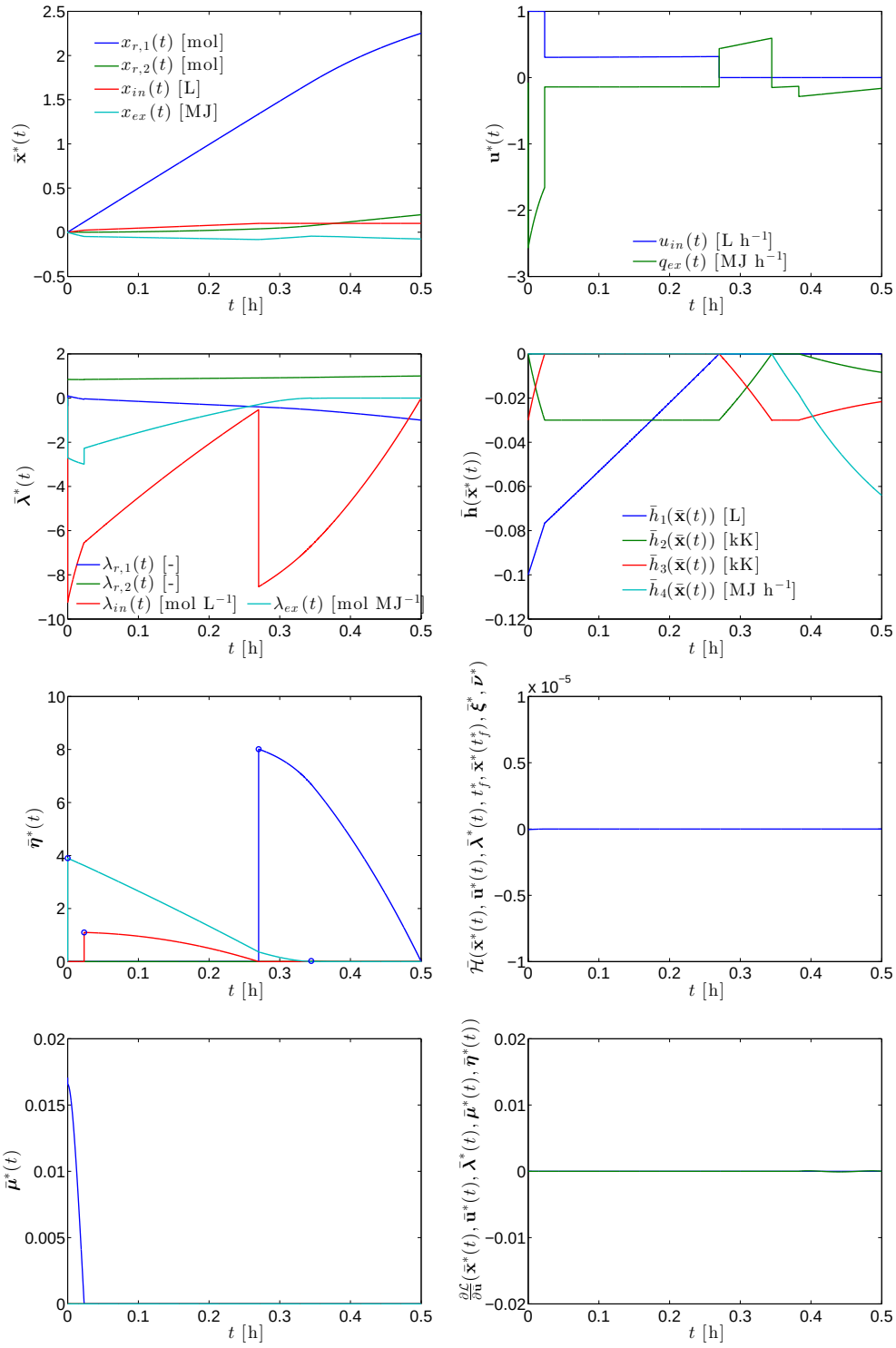

Figure 8.7 – Trajectories of the states, inputs, adjoint variables, Lagrange multipliers, reformulated Hamiltonian function and stationarity conditions for the optimal solution to Problem (8.83) with the parsimonious input parameterization and the description of the sensitivity-seeking input arc using cubic splines.

It is also possible to observe that the remaining necessary conditions of optimality are fully satisfied since $\bar{\mathscr{H}}\left(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t), \bar{\boldsymbol{\lambda}}^*(t), t_f^*, \bar{\mathbf{x}}^*(t_f^*), \bar{\boldsymbol{\xi}}^*, \bar{\boldsymbol{\nu}}^*\right)$ satisfies the condition in Eq. (G.20), $\frac{\partial \mathscr{L}}{\partial \bar{\mathbf{u}}}\left(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t), \bar{\boldsymbol{\lambda}}^*(t), \bar{\boldsymbol{\mu}}^*(t), \bar{\boldsymbol{\eta}}^*(t)\right)$ satisfies the condition in Eq. (G.26), and $\bar{\boldsymbol{\mu}}^*(t)$ and $\bar{\mathbf{g}}\left(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\right)$ (inferred from $\mathbf{u}^*(t)$) satisfy the conditions in Eqs. (G.27)–(G.29). Additionally, $\bar{\boldsymbol{\eta}}^*(t)$ and $\bar{\mathbf{h}}\left(\bar{\mathbf{x}}^*(t)\right)$ satisfy the conditions in Eqs. (G.30)–(G.34), and, at the entry points θ (whose values $\bar{\boldsymbol{\pi}}^*(\theta)$ are indicated by circles that coincide with the corresponding values of $\bar{\boldsymbol{\eta}}^*(\theta)$), the conditions in Eqs. (G.17)–(G.18) are also satisfied.

8.6 Conclusion

This chapter has presented a parsimonious input parameterization that describes the optimal input quite accurately with fewer parameters than direct methods for a generic class of dynamic optimization problems, thereby reducing the number of decision variables and making it a valid candidate for global dynamic optimization and dynamic real-time optimization. At the same time, the resulting dynamic optimization method retains the attractive features of direct sequential methods, that is, the ability to compute the terminal costs and constraints and their derivatives with respect to the decision variables via numerical integration of ordinary differential equations.

This parameterization relies on the formulation of adjoint-free optimal control laws for each arc in the sequences that compose the optimal inputs, with these optimal inputs being described as functions of the states and the inputs, and not as a function of any adjoint variables. These adjoint-free optimal control laws are generated for two different types of arcs: (i) constraint-seeking arcs, where the control laws result from the constraints; and (ii) sensitivity-seeking arcs, where the control laws are analytically computed from the system dynamics or are determined by a description using cubic splines. In the case of batch, semi-batch and continuous reactors, the analytical description of sensitivity-seeking optimal control laws is enabled by the representation of the dynamic model in terms of extents. Subsequently, this method can also be used to automatically generate solutions that satisfy the Pontryagin's maximum principle.

The goal of this chapter has not been to present a full procedure for global dynamic optimization and dynamic real-time optimization, but rather to argue that a careful choice of the input parameterization is important for global dynamic optimization and dynamic real-time optimization since their efficiency strongly depends on the number of decision variables. In summary, this method, which is based on the enumeration of a finite number of arc sequences that may appear in the solution to a given problem, corresponds to a novel approach that aims at finding the global solution to dynamic optimization problems even in the presence of plant-model mismatch.

In future work, it would be useful to be able to express the terminal cost and constraints of the dynamic optimization problems as explicit polynomial functions of the decision variables, which is typically required by global optimization algorithms. After achieving this goal, the performance of this approach for global dynamic optimization will be assessed

and compared to existing approaches, and its connection with other methods that enforce convergence to the plant optimum will be investigated.

9 Conclusion

9.1 Final Remarks

This thesis has presented the concepts of variants and invariants for lumped reaction systems, and in particular the concept of extents, in Chapter 2, and it has generalized the concept of extents to distributed reaction systems in Chapter 3. Then, these concepts have been applied to estimation, control, and optimization of reaction systems. In Chapter 4, the concept of extents has been used for estimation of kinetic parameters via the extent-based incremental approach, while in Chapter 5 the concept of variants has been used for estimation of unknown rate signals without identification of kinetic models. Then, in Chapter 6, the concept of extents has been applied to efficient reactor control with kinetic models, and the estimation of unknown rate signals has been used to implement control in the absence of kinetic models, while Chapter 7 has taken advantage of feedback control and estimation of unknown rate signals to speed up the estimation of plant steady state and the steady-state optimization of imperfectly known dynamic systems. Finally, the concept of extents has been used in Chapter 8 to convert the model of several reactors to a framework that allows the computation of optimal control laws for dynamic optimization problems so as to provide a more efficient parameterization of the optimal inputs. From this summary, it is clear that the applications of the concept of variants and invariants encompass model-based applications, as in Chapters 4, 6, and 8, and data-driven applications, as in Chapters 5, 6, and 7.

The next paragraphs summarize the main conclusions of the chapters in this thesis.

Chapter 2: Concept of Variants and Invariants for Lumped Reaction Systems This chapter has presented the dynamic models of several lumped reaction systems in terms of material balances described by the numbers of moles and heat balances described by the heat. Then, several transformations between the original states related to the numbers of moles and different concepts of variants and invariants have been detailed for the case of homogeneous reaction systems. In addition, the concept of extents and the transformations between numbers of moles and extents have been shown for the cases of reaction systems

with instantaneous equilibria, multiphase reaction systems, and reaction systems with heat balance. Although the concepts of variants and invariants and the transformations to and from variants and invariants were already known for all these lumped reaction systems prior to this thesis, this chapter has summarized this knowledge and presented a complete and systematic overview of these concepts.

Chapter 3: Concept of Extents for Distributed Reaction Systems This chapter has generalized the concept of extents and the transformation to extents to generic distributed reaction systems that include tubular reactors and reactive separation columns. Each extent in a distributed reaction system describes uniquely and completely a particular rate process, taking into account the amount that has been transported by advection to a farther position and that has been removed by an outlet. The definition of extents, as well as the linear transformations between original concentration variables and extents, are similar to the case of vessel extents for lumped reaction systems. The generalization of the concept of extents to distributed reaction systems opens up new perspectives for industrially relevant applications for distributed reaction systems. These perspectives for applications of the concept of extents in distributed reaction systems are justified by the fact that some of these applications have been investigated for lumped reaction systems.

Chapter 4: Estimation of Kinetic Parameters via the Incremental Approach This chapter has shown that the extent-based incremental approach for model identification and estimation of kinetic parameters can be used not only to converge efficiently to global optimality, but also to provide maximum-likelihood parameter estimates, with quality similar to simultaneous model identification. The cost function that results from this approach involves only the parameters of a single rate candidate and is a quadratic function of the parameters in which the rate expression is linear, which means that this cost function can be approximated via a Taylor series expansion as a rational function of the parameters that appear nonlinearly in the rate expression. The resulting polynomial optimization problem can be converted to an SDP, which can be handled by solvers that efficiently attain the global solution upon convergence. Furthermore, maximum-likelihood parameter estimation relies on a method to compute uncorrelated experimental extents from measured concentrations, and a method to obtain unbiased rate estimates computed from measurements, resulting in modeled extents that correspond to the integral of unbiased rate estimates.

Chapter 5: Estimation of Rate Signals without Kinetic Models This chapter has shown how to compute unknown rates from the available measurements, using knowledge about the structural relationship between the available states and the unknown and available rates. The unknown rates are estimated via numerical differentiation of variants that are computed from available states via an appropriate linear transformation, without the use of any rate model. These variants depend on the unknown rates. Only one parameter needs to be tuned, the parameter of the differentiation filter. The implications of rate estimation

with respect to control without kinetic models and estimation of plant steady state have been presented in the following two chapters.

Chapter 6: Reactor Control This chapter has considered reactor control with and without kinetic models, in both cases using the concept of variants and invariants. The first part of this chapter has proposed a control scheme via feedback linearization in the presence of a kinetic model, which achieves offset-free control of a subset of the states and sets the closed-loop time constants of all the states that describe the reaction system. The second part of this chapter has considered the control of a subset of the available states of a generic system without the knowledge of a rate model, based on the structural information about the dynamic relationship between the states and rates in the system. This controller is based on feedback linearization and estimation of the unknown rates, and requires few conditions and tunable parameters in addition to the ones needed for rate estimation. This control scheme simplifies significantly MIMO control design, allows forcing the control error to decay exponentially to zero, and eliminates the steady-state error even without any integral component. This controller can outperform PI control for the purpose of disturbance rejection and setpoint tracking in a realistic reactor control problem.

Chapter 7: Fast Steady-state Optimization of Dynamic Systems This chapter has presented a novel method that uses feedback control and measurement-based rate estimation to estimate the plant steady state before the plant reaches steady state. This approach is possible for systems where some of the states do not affect the other states. In the context of real-time optimization, this implies that each iteration takes less time, which means that the time needed to drive the plant to optimality will be shorter. With this approach, certain fast states are driven quickly to steady state via feedback control, and the cost and constraint functions of the RTO problem are expressed in terms of the fast states, typically involving certain rates that depend only on fast states. The rates are estimated from output measurements, without the use of rate models, as soon as their steady-state values have been reached. The decision variables of the RTO problem correspond to setpoints of the controlled plant. Currently, the applicability of this approach is limited by its sensitivity to noise and the difficulty of tuning certain parameters.

Chapter 8: Dynamic Optimization via Parsimonious Input Parameterization This chapter has presented a parsimonious input parameterization that describes the optimal input quite accurately with fewer parameters than direct methods for a generic class of dynamic optimization problems. Adjoint-free optimal control laws are computed for each arc in the sequences that compose the optimal inputs, where these arcs can be of two different types: (i) constraint-seeking arcs, where the control laws result from the constraints; and (ii) sensitivity-seeking arcs, where the control laws are analytically computed from the system dynamics or are determined by a description using cubic splines. In the case of the analytical description of sensitivity-seeking optimal control laws for batch, semi-batch and

continuous reactors, this description takes advantage of the representation of the dynamic model in terms of extents. The implications of this approach and possible future extensions for global dynamic optimization and dynamic real-time optimization have been discussed.

9.2 Outlook and Perspectives

Although this thesis has consolidated and generalized the concept of variants and invariants, particularly the concept of extents, and investigated novel applications to estimation, control, and optimization of reaction systems, several extensions can be envisaged at this point. This section explores some directions for future work on the concept and applications of variants and invariants.

Interconnected and plant-wide systems The extension of the concept of variants and invariants and its application to interconnected and plant-wide systems was one of the original objectives of this doctoral work. These systems are composed of more than one unit operation, in contrast to the systems considered in this thesis, which only included the reactor as a single unit operation. For example, a simple proof of concept would consist in a system composed of a reactor, a simple separation system, such as a flash column, and a recycling loop for a part of the outlet stream into the reactor. In particular, it would be useful to investigate whether variants and invariants can be used to describe links between different units, for example in the form of extents of recycling, or to decouple dynamic effects in unit operations in series or in parallel, and in which conditions this is possible. The objective would be to simplify the understanding of networks and plant-wide systems, and to provide new tools for process intensification, for example.

This topic has been the object of research during this doctoral work. However, it was found that, although the concept of variant and invariant states can be easily extended to simple systems, such as a reactor connected to a flash unit, it is not yet clear how the application of variants and invariants could be helpful to improve the analysis of these simple systems with respect to the analysis that can be done using the original states (concentrations or numbers of moles). This lack of incentive arises from the fact that, in processing units without reaction, the dynamic effects are already decoupled. This indicates that the concept of variants and invariants is most useful for unit operations with reactions that affect several states in the original representation of the system.

Nevertheless, the analysis of this extension to interconnected and plant-wide systems from a different angle or with a specific application in mind might yield more interesting results. It is also worth mentioning that the field of distributed and interconnected network systems has recently received much attention from the scientific community working on control, which may generate future interest in the network systems that are typically found in the chemical and biotechnological industries.

Reaction systems described by population balances A relevant class of reaction systems that has not been investigated using the concept of variants and invariants corresponds to the reaction systems described by population balances, which are very common in the case of polymerization reactions. In these reaction systems, instead of a finite and typically small number of species, there is a potentially infinite number of species with a distribution of different molecular weights, which can be generated from one another by adding or removing monomers from their structure. These reaction systems are typically described by partial differential equations even in the case of lumped reaction systems.

Although this class of reaction systems has not been investigated, it is likely that the concept of variants and invariants and its application to model identification for reaction systems described by population balances can be extended in a relatively simple way from the concept of extents and its application to model identification for distributed reaction systems, which are also described by partial differential equations.

Systems with more balance equations than rates This thesis has focused on the development and application of the concept of variants and invariants to reaction systems. However, in principle, the same concept exists for any system with a similar structure. This structure is valid for any system described by balance equations with several dynamic effects or rates that affect various states simultaneously, especially if the number of balance equations is greater than the number of rates. For any system with this structure, the extension of the concept of variants and invariants and its applications presented in this thesis would be straightforward. In fact, all the developments in this thesis for data-driven applications (namely rate estimation, control, and steady-state optimization) have already used a generic formulation that would allow their immediate use for any system with this structure.

Hence, an interesting task for future work would be to conduct a survey of the dynamic systems that are known in different fields of engineering or even other disciplines, with the goal of finding new classes of dynamic systems that share the same properties. Then, it would also be interesting to assess whether there exist unsolved problems related to these classes of dynamic systems that could benefit from the developments made in the context of reaction systems, and conversely, whether the investigation of other classes of dynamic systems can be helpful in the context of reaction systems, or even to obtain new ideas about relevant research topics in the field of dynamic systems.

Optimization Prior to this doctoral work, very few applications of variants and invariants to optimization had been reported. In this thesis, applications to both steady-state and dynamic optimization have been developed, in the former case without the use of kinetic models, and in the latter case with the use of kinetic models. Furthermore, the application of the concept of extents to estimation of kinetic parameters also had some interesting consequences with respect to the simplification and global optimality of the solution to the underlying optimization problems. These facts open up new perspectives for research of new applications of the concept of variants and invariants to optimization.

A Appendix of Chapter 2

A.1 Decomposition of Matrices with Linearly Dependent Rows

The two methods to decompose matrices with linearly dependent rows proceed as follows:

1. Let us suppose that it is previously known or it is found through computation that there exists an $R_d \times (R_d - R_s)$ matrix $\mathbf{K}_s$ of rank $R_d - R_s$ with columns that are a basis of the null space of $\mathbf{M}_d^{\mathrm{T}}$, that is,

$$\mathbf{K}_s^{\mathrm{T}}\mathbf{M}_d = \mathbf{K}_s^{\mathrm{T}}\mathbf{L}_s\mathbf{M} = \mathbf{0}_{(R_d-R_s)\times C}. \tag{A.1}$$

Since $\mathbf{M}$ has full row rank, the previous condition implies that

$$\mathbf{K}_s^{\mathrm{T}}\mathbf{L}_s = \mathbf{0}_{(R_d-R_s)\times R_s}, \tag{A.2}$$

which means that the columns of $\mathbf{L}_s$ are a basis of the null space of $\mathbf{K}_s^{\mathrm{T}}$. Now, note that any matrix $\hat{\mathbf{L}}_s$ with columns that are a basis of the null space of $\mathbf{K}_s^{\mathrm{T}}$ satisfies the condition

$$\hat{\mathbf{L}}_s = \mathbf{L}_s\hat{\mathbf{V}}_s, \tag{A.3}$$

where $\hat{\mathbf{V}}_s$ is an invertible $R_s \times R_s$ matrix. Then, if one chooses

$$\hat{\mathbf{M}} = \left(\hat{\mathbf{L}}_s^{\mathrm{T}}\hat{\mathbf{L}}_s\right)^{-1}\hat{\mathbf{L}}_s^{\mathrm{T}}\mathbf{M}_d, \tag{A.4}$$

which also implies that

$$\hat{\mathbf{M}} = \left(\hat{\mathbf{L}}_s^{\mathrm{T}}\hat{\mathbf{L}}_s\right)^{-1}\hat{\mathbf{L}}_s^{\mathrm{T}}\hat{\mathbf{L}}_s\hat{\mathbf{V}}_s^{-1}\mathbf{M} = \hat{\mathbf{V}}_s^{-1}\mathbf{M} \tag{A.5}$$

is of full row rank, one can show that the rows $\hat{\mathbf{M}}$ are correct candidates for the linearly

independent rows since

$$\hat{\mathbf{L}}_s\hat{\mathbf{M}} = \hat{\mathbf{L}}_s\hat{\mathbf{V}}_s^{-1}\mathbf{M} = \mathbf{M}_d. \tag{A.6}$$

2. Another possibility is to guess that the rows of $\mathbf{M}_d$ are a linear combination of the R_s linearly independent rows specified by a matrix $\hat{\mathbf{M}}$ of rank R_s, which can be written as

$$\mathbf{M}_d = \hat{\mathbf{L}}_s\hat{\mathbf{M}}, \tag{A.7}$$

for some $R_d \times R_s$ matrix $\hat{\mathbf{L}}_s$ of rank R_s.
If this guess is correct, then $\hat{\mathbf{L}}_s$ is of full column rank and is given by

$$\hat{\mathbf{L}}_s = \mathbf{M}_d\hat{\mathbf{M}}^{\mathrm{T}}\left(\hat{\mathbf{M}}\hat{\mathbf{M}}^{\mathrm{T}}\right)^{-1}, \tag{A.8}$$

which means that one can verify if the guess is correct by checking if the condition

$$\mathbf{M}_d = \mathbf{M}_d\hat{\mathbf{M}}^{\mathrm{T}}\left(\hat{\mathbf{M}}\hat{\mathbf{M}}^{\mathrm{T}}\right)^{-1}\hat{\mathbf{M}} \tag{A.9}$$

holds. In that case, the matrix $\hat{\mathbf{M}}$ satisfies the condition

$$\hat{\mathbf{M}} = \hat{\mathbf{V}}_s^{-1}\mathbf{M}, \tag{A.10}$$

where $\hat{\mathbf{V}}_s$ is an invertible $R_s \times R_s$ matrix, which also implies that

$$\hat{\mathbf{L}}_s = \mathbf{L}_s\hat{\mathbf{V}}_s\hat{\mathbf{M}}\hat{\mathbf{M}}^{\mathrm{T}}\left(\hat{\mathbf{M}}\hat{\mathbf{M}}^{\mathrm{T}}\right)^{-1} = \mathbf{L}_s\hat{\mathbf{V}}_s. \tag{A.11}$$

A.2 Equivalence of Descriptions of Reaction Systems with Instantaneous Equilibria

This section shows that the model of reaction systems with instantaneous equilibria described by the system of DAEs given by the differential equations (2.56) and (2.62) and algebraic equations (2.54), (2.55) and (2.61) is equivalent to the description obtained via differentiation of Eq. (2.54). For the sake of simplicity, the dependence on time is omitted.

The algebraic equations (2.54), (2.55) and (2.61) enforce the following constraint implicitly:

$$\begin{bmatrix} \mathbf{0}_{R_e} \\ \dot{\mathbf{n}}_s \\ \dot{Q}_s \end{bmatrix} = \begin{bmatrix} \frac{\partial \boldsymbol{\varphi}_e}{\partial \mathbf{n}}(\mathbf{n}, Q) & \frac{\partial \boldsymbol{\varphi}_e}{\partial Q}(\mathbf{n}, Q) \\ \mathbf{P}_e^{\mathrm{T}} & \mathbf{0}_{S_s} \\ \Delta\mathbf{H}_e^{\mathrm{T}} & 1 \end{bmatrix} \begin{bmatrix} \dot{\mathbf{n}} \\ \dot{Q} \end{bmatrix}. \tag{A.12}$$

Furthermore, the differential equations (2.56) and (2.62) imply that

$$\begin{bmatrix} \mathbf{0}_{R_e} \\ \dot{\mathbf{n}}_s \\ \dot{Q}_s \end{bmatrix} = \begin{bmatrix} \mathbf{0}_{R_e \times S} & \mathbf{0}_{R_e} \\ \mathbf{P}_e^{\mathrm{T}} & \mathbf{0}_{S_s} \\ \Delta \mathbf{H}_e^{\mathrm{T}} & 1 \end{bmatrix} \begin{bmatrix} \boldsymbol{\phi}_s - \omega \mathbf{n} \\ \psi_s - \omega Q \end{bmatrix}. \tag{A.13}$$

This means that the system of DAEs enforces the following constraint implicitly:

$$\begin{bmatrix} \dot{\mathbf{n}} \\ \dot{Q} \end{bmatrix} = \begin{bmatrix} \frac{\partial \boldsymbol{\varphi}_e}{\partial \mathbf{n}}(\mathbf{n}, Q) & \frac{\partial \boldsymbol{\varphi}_e}{\partial Q}(\mathbf{n}, Q) \\ \mathbf{P}_e^{\mathrm{T}} & \mathbf{0}_{S_s} \\ \Delta \mathbf{H}_e^{\mathrm{T}} & 1 \end{bmatrix}^{-1} \begin{bmatrix} \mathbf{0}_{R_e \times S} & \mathbf{0}_{R_e} \\ \mathbf{P}_e^{\mathrm{T}} & \mathbf{0}_{S_s} \\ \Delta \mathbf{H}_e^{\mathrm{T}} & 1 \end{bmatrix} \begin{bmatrix} \boldsymbol{\phi}_s - \omega \mathbf{n} \\ \psi_s - \omega Q \end{bmatrix}. \tag{A.14}$$

On the other hand, from Eqs. (2.50) and (2.57) and differentiation of Eq. (2.54), it would be known that

$$\mathbf{0}_{R_e} = \frac{\partial \boldsymbol{\varphi}_e}{\partial \mathbf{z}}(\mathbf{n}, Q) \left(\begin{bmatrix} \mathbf{N}_e^{\mathrm{T}} \\ -\Delta \mathbf{H}_{r,e}^{\mathrm{T}} \end{bmatrix} \frac{V}{\epsilon} \boldsymbol{\varphi}_e(\mathbf{n}, Q) + \begin{bmatrix} \boldsymbol{\phi}_s - \omega \mathbf{n} \\ \psi_s - \omega Q \end{bmatrix} \right), \tag{A.15}$$

which implies that

$$\frac{V}{\epsilon} \boldsymbol{\varphi}_e(\mathbf{n}, Q) = - \left(\frac{\partial \boldsymbol{\varphi}_e}{\partial \mathbf{z}}(\mathbf{n}, Q) \begin{bmatrix} \mathbf{N}_e^{\mathrm{T}} \\ -\Delta \mathbf{H}_{r,e}^{\mathrm{T}} \end{bmatrix} \right)^{-1} \frac{\partial \boldsymbol{\varphi}_e}{\partial \mathbf{z}}(\mathbf{n}, Q) \begin{bmatrix} \boldsymbol{\phi}_s - \omega \mathbf{n} \\ \psi_s - \omega Q \end{bmatrix}, \tag{A.16}$$

provided that $\frac{\partial \boldsymbol{\varphi}_e}{\partial \mathbf{z}}(\mathbf{n}, Q) \begin{bmatrix} \mathbf{N}_e^{\mathrm{T}} \\ -\Delta \mathbf{H}_{r,e}^{\mathrm{T}} \end{bmatrix}$ is nonsingular.

If this equation is replaced into Eqs. (2.50) and (2.57), it yields the following result:

$$\begin{bmatrix} \dot{\mathbf{n}} \\ \dot{Q} \end{bmatrix} = \left(\mathbf{I}_{S+1} - \begin{bmatrix} \mathbf{N}_e^{\mathrm{T}} \\ -\Delta \mathbf{H}_{r,e}^{\mathrm{T}} \end{bmatrix} \left(\frac{\partial \boldsymbol{\varphi}_e}{\partial \mathbf{z}}(\mathbf{n}, Q) \begin{bmatrix} \mathbf{N}_e^{\mathrm{T}} \\ -\Delta \mathbf{H}_{r,e}^{\mathrm{T}} \end{bmatrix} \right)^{-1} \frac{\partial \boldsymbol{\varphi}_e}{\partial \mathbf{z}}(\mathbf{n}, Q) \right) \begin{bmatrix} \boldsymbol{\phi}_s - \omega \mathbf{n} \\ \psi_s - \omega Q \end{bmatrix}. \tag{A.17}$$

Hence, the two descriptions in Eqs. (A.14) and (A.17) are equivalent since

$$\begin{aligned} &\begin{bmatrix} \frac{\partial \boldsymbol{\varphi}_e}{\partial \mathbf{n}}(\mathbf{n}, Q) & \frac{\partial \boldsymbol{\varphi}_e}{\partial Q}(\mathbf{n}, Q) \\ \mathbf{P}_e^{\mathrm{T}} & \mathbf{0}_{S_s} \\ \Delta \mathbf{H}_e^{\mathrm{T}} & 1 \end{bmatrix}^{-1} \begin{bmatrix} \mathbf{0}_{R_e \times S} & \mathbf{0}_{R_e} \\ \mathbf{P}_e^{\mathrm{T}} & \mathbf{0}_{S_s} \\ \Delta \mathbf{H}_e^{\mathrm{T}} & 1 \end{bmatrix} \\ &= \mathbf{I}_{S+1} - \begin{bmatrix} \frac{\partial \boldsymbol{\varphi}_e}{\partial \mathbf{n}}(\mathbf{n}, Q) & \frac{\partial \boldsymbol{\varphi}_e}{\partial Q}(\mathbf{n}, Q) \\ \mathbf{P}_e^{\mathrm{T}} & \mathbf{0}_{S_s} \\ \Delta \mathbf{H}_e^{\mathrm{T}} & 1 \end{bmatrix}^{-1} \begin{bmatrix} \frac{\partial \boldsymbol{\varphi}_e}{\partial \mathbf{z}}(\mathbf{n}, Q) \\ \mathbf{0}_{S_s \times (S+1)} \\ \mathbf{0}_{S+1}^{\mathrm{T}} \end{bmatrix} \\ &= \mathbf{I}_{S+1} - \begin{bmatrix} \mathbf{N}_e^{\mathrm{T}} \\ -\Delta \mathbf{H}_{r,e}^{\mathrm{T}} \end{bmatrix} \left(\frac{\partial \boldsymbol{\varphi}_e}{\partial \mathbf{z}}(\mathbf{n}, Q) \begin{bmatrix} \mathbf{N}_e^{\mathrm{T}} \\ -\Delta \mathbf{H}_{r,e}^{\mathrm{T}} \end{bmatrix} \right)^{-1} \frac{\partial \boldsymbol{\varphi}_e}{\partial \mathbf{z}}(\mathbf{n}, Q). \end{aligned} \tag{A.18}$$

A.3 Number of Vessel Extents in Open Homogeneous Reactors

This section shows that the numbers of moles can be computed as a linear transformation of less than $R + p + 1$ vessel extents in some particular cases of open homogeneous reactors. Two relevant examples of these particular cases are the CSTRs with constant density or with an ideal mixture and the open homogeneous reactors with initial conditions that correspond to a steady state.

A.3.1 CSTR with constant density or with an ideal mixture

This section shows that, not only for the case of a homogeneous CSTR with constant density but also for a homogeneous CSTR with an ideal mixture, the inverse of the residence time is a linear combination of reaction rates and inlet flowrates.

Proposition A.1. *For any homogeneous CSTR with S species, R independent reactions and p independent inlets that contains an ideal mixture (such that the volume of the mixture is the sum of the volumes of each pure species), the inverse of the residence time $\omega(t)$ is the linear combination of reaction rates and inlet flowrates*

$$\omega(t) = \mathbf{k}_r^{\mathrm{T}} \mathbf{r}_v(t) + \mathbf{k}_{in}^{\mathrm{T}} \mathbf{u}_{in}(t), \tag{A.19}$$

with

$$\mathbf{k}_r^{\mathrm{T}} = \frac{\mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \mathbf{n}_0} \mathbf{N}^{\mathrm{T}}, \tag{A.20}$$

$$\mathbf{k}_{in}^{\mathrm{T}} = \frac{\mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \mathbf{n}_0} \mathbf{W}_{in}, \tag{A.21}$$

where $\boldsymbol{\rho}$ is the diagonal matrix of densities.

Proof. In a reactor with an ideal mixture, one can assume that the volume $V(t)$ is given by

$$V(t) = \mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \mathbf{n}(t), \tag{A.22}$$

and, since the volume is constant in a CSTR,

$$\mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \mathbf{n}(t) = \mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \mathbf{n}_0. \tag{A.23}$$

This implies that the inverse of the residence time must be given by

$$\omega(t) = \frac{\mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \mathbf{n}_0} \left(\mathbf{N}^{\mathrm{T}} \mathbf{r}_v(t) + \mathbf{W}_{in} \mathbf{u}_{in}(t) \right), \tag{A.24}$$

to keep the volume constant, as follows:

$$\begin{aligned} 0 &= \mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \dot{\mathbf{n}}(t) \\ &= \mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \left(\mathbf{N}^{\mathrm{T}} \mathbf{r}_v(t) + \mathbf{W}_{in} \mathbf{u}_{in}(t) - \omega(t) \mathbf{n}(t) \right) \\ &= \mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \left(\mathbf{N}^{\mathrm{T}} \mathbf{r}_v(t) + \mathbf{W}_{in} \mathbf{u}_{in}(t) \right) - \mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \mathbf{n}_0 \omega(t). \end{aligned} \tag{A.25}$$

□

Remark A.1. In a reactor with constant density, the volume is given by a particular case of the equation that gives the volume of a reactor with an ideal mixture, if one replaces $\boldsymbol{\rho}$ by $\rho \mathbf{I}_S$. Since

$$\mathbf{1}_S^{\mathrm{T}} \mathbf{M}_w \mathbf{N}^{\mathrm{T}} = \mathbf{0}_R^{\mathrm{T}}, \tag{A.26}$$

$$\mathbf{1}_S^{\mathrm{T}} \mathbf{M}_w \mathbf{W}_{in} = \mathbf{1}_p^{\mathrm{T}}, \tag{A.27}$$

$$\mathbf{1}_S^{\mathrm{T}} \mathbf{M}_w \mathbf{n}_0 = m_0, \tag{A.28}$$

the inverse of the residence time $\omega(t)$ is given by Eq. (A.19), with Eqs. (A.20) and (A.21) being replaced by

$$\mathbf{k}_r^{\mathrm{T}} = \mathbf{0}_R^{\mathrm{T}}, \tag{A.29}$$

$$\mathbf{k}_{in}^{\mathrm{T}} = \frac{\mathbf{1}_p^{\mathrm{T}}}{m_0}. \tag{A.30}$$

A.3.2 Initial conditions and steady state

This section shows that, for any open homogeneous reactor, the numbers of moles are a linear transformation of only $R + p$ vessel extents if the initial conditions are a linear combination of the stoichiometries and of the inlet compositions, and, in particular, if these initial conditions correspond to a steady state.

Proposition A.2. *For any open homogeneous reactor with S species, R independent reactions, p independent inlets and one outlet whose initial numbers of moles are given by the linear combination*

$$\mathbf{n}_0 = \mathbf{N}^{\mathrm{T}} \mathbf{v}_r + \mathbf{W}_{in} \mathbf{v}_{in}, \tag{A.31}$$

the numbers of moles are the linear transformation of R vessel extents of reaction $\mathbf{x}_r(t)$ *and p vessel extents of inlet* $\mathbf{x}_{in}(t)$

$$\mathbf{n}(t) = \mathbf{N}^{\mathrm{T}} \mathbf{x}_r(t) + \mathbf{W}_{in} \mathbf{x}_{in}(t), \tag{A.32}$$

where the vessel extents are described by the ODEs

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t), \qquad \mathbf{x}_r(0) = \mathbf{v}_r, \tag{A.33}$$

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) - \omega(t)\mathbf{x}_{in}(t), \quad \mathbf{x}_{in}(0) = \mathbf{v}_{in}. \tag{A.34}$$

In particular, if the numbers of moles are initially at steady state $\bar{\mathbf{n}}_0$*, then*

$$\mathbf{x}_r(0) = \mathbf{v}_r = \frac{\bar{\mathbf{r}}_v}{\bar{\omega}}, \tag{A.35}$$

$$\mathbf{x}_{in}(0) = \mathbf{v}_{in} = \frac{\bar{\mathbf{u}}_{in}}{\bar{\omega}}, \tag{A.36}$$

with $\bar{\mathbf{r}}_v$*,* $\bar{\mathbf{u}}_{in}$ *and* $\bar{\omega}$ *the reaction rates, inlet flowrates and inverse of the residence time at steady state.*

Proof. This proposition can be proven by checking the consistency of the initial conditions

$$\begin{aligned}\mathbf{n}(0) &= \mathbf{N}^{\mathrm{T}}\mathbf{x}_r(0) + \mathbf{W}_{in}\mathbf{x}_{in}(0)\\ &= \mathbf{N}^{\mathrm{T}}\mathbf{v}_r + \mathbf{W}_{in}\mathbf{v}_{in}\\ &= \mathbf{n}_0,\end{aligned} \tag{A.37}$$

and ODEs

$$\begin{aligned}\dot{\mathbf{n}}(t) &= \mathbf{N}^{\mathrm{T}}\dot{\mathbf{x}}_r(t) + \mathbf{W}_{in}\dot{\mathbf{x}}_{in}(t)\\ &= \mathbf{N}^{\mathrm{T}}\left(\mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t)\right) + \mathbf{W}_{in}\left(\mathbf{u}_{in}(t) - \omega(t)\mathbf{x}_{in}(t)\right)\\ &= \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}\mathbf{u}_{in}(t) - \omega(t)\mathbf{N}^{\mathrm{T}}\mathbf{x}_r(t) - \omega(t)\mathbf{W}_{in}\mathbf{x}_{in}(t)\\ &= \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}(t).\end{aligned} \tag{A.38}$$

Finally, let us note that, at steady state,

$$\mathbf{0}_S = \mathbf{N}^{\mathrm{T}}\bar{\mathbf{r}}_v + \mathbf{W}_{in}\bar{\mathbf{u}}_{in} - \bar{\omega}\bar{\mathbf{n}}_0, \tag{A.39}$$

which implies that

$$\bar{\mathbf{n}}_0 = \mathbf{N}^{\mathrm{T}}\frac{\bar{\mathbf{r}}_v}{\bar{\omega}} + \mathbf{W}_{in}\frac{\bar{\mathbf{u}}_{in}}{\bar{\omega}}. \tag{A.40}$$

□

A.3.3 Constrained outlet

This section shows that, for any open homogeneous reactor where the inverse of the residence time is a linear combination of reaction rates and inlet flowrates, the numbers of moles are a linear transformation of $R + p$ vessel extents, or only $R + p - 1$ vessel extents if the initial conditions are at steady state, and these linear transformations can be obtained

in the case of any homogeneous CSTR with an ideal mixture or with constant density.

Proposition A.3. *For any open homogeneous reactor with S species, R independent reactions, p independent inlets and one outlet where the inverse of the residence time is the linear combination of reaction rates and inlet flowrates*

$$\omega(t) = \mathbf{k}_r^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{k}_{in}^{\mathrm{T}}\mathbf{u}_{in}(t), \tag{A.41}$$

the numbers of moles are the linear transformation of R vessel extents of reaction $\mathbf{x}_r(t)$ *and p vessel extents of inlet* $\mathbf{x}_{in}(t)$

$$\mathbf{n}(t) = \left(\mathbf{N}^{\mathrm{T}} - \mathbf{n}_0\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{x}_r(t) + \left(\mathbf{W}_{in} - \mathbf{n}_0\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{x}_{in}(t) + \mathbf{n}_0, \tag{A.42}$$

where the vessel extents are described by the ODEs

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t), \qquad \mathbf{x}_r(0) = \mathbf{0}_R, \tag{A.43}$$

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) - \omega(t)\mathbf{x}_{in}(t), \quad \mathbf{x}_{in}(0) = \mathbf{0}_p. \tag{A.44}$$

Proof. This proposition can be proven by checking the consistency of the initial conditions

$$\begin{aligned}\mathbf{n}(0) &= \left(\mathbf{N}^{\mathrm{T}} - \mathbf{n}_0\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{x}_r(0) + \left(\mathbf{W}_{in} - \mathbf{n}_0\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{x}_{in}(0) + \mathbf{n}_0 \\ &= \mathbf{n}_0,\end{aligned} \tag{A.45}$$

and ODEs

$$\begin{aligned}\dot{\mathbf{n}}(t) &= \left(\mathbf{N}^{\mathrm{T}} - \mathbf{n}_0\mathbf{k}_r^{\mathrm{T}}\right)\dot{\mathbf{x}}_r(t) + \left(\mathbf{W}_{in} - \mathbf{n}_0\mathbf{k}_{in}^{\mathrm{T}}\right)\dot{\mathbf{x}}_{in}(t) \\ &= \left(\mathbf{N}^{\mathrm{T}} - \mathbf{n}_0\mathbf{k}_r^{\mathrm{T}}\right)\left(\mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t)\right) + \left(\mathbf{W}_{in} - \mathbf{n}_0\mathbf{k}_{in}^{\mathrm{T}}\right)\left(\mathbf{u}_{in}(t) - \omega(t)\mathbf{x}_{in}(t)\right) \\ &= \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}\mathbf{u}_{in}(t) - \mathbf{n}_0\left(\mathbf{k}_r^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{k}_{in}^{\mathrm{T}}\mathbf{u}_{in}(t)\right) \\ &\quad - \omega(t)\left(\mathbf{N}^{\mathrm{T}} - \mathbf{n}_0\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{x}_r(t) - \omega(t)\left(\mathbf{W}_{in} - \mathbf{n}_0\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{x}_{in}(t) \\ &= \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}\mathbf{u}_{in}(t) \\ &\quad - \omega(t)\left(\mathbf{N}^{\mathrm{T}} - \mathbf{n}_0\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{x}_r(t) - \omega(t)\left(\mathbf{W}_{in} - \mathbf{n}_0\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{x}_{in}(t) - \omega(t)\mathbf{n}_0 \\ &= \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}(t).\end{aligned} \tag{A.46}$$

□

Proposition A.4. *For any homogeneous CSTR with S species, R independent reactions and p independent inlets that contains an ideal mixture, the numbers of moles are the linear transformation of R vessel extents of reaction* $\mathbf{x}_r(t)$ *and p vessel extents of inlet* $\mathbf{x}_{in}(t)$

$$\mathbf{n}(t) = \left(\mathbf{I}_S - \frac{\mathbf{n}_0\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w\mathbf{n}_0}\right)\left(\mathbf{N}^{\mathrm{T}}\mathbf{x}_r(t) + \mathbf{W}_{in}\mathbf{x}_{in}(t)\right) + \mathbf{n}_0, \tag{A.47}$$

where the vessel extents are described by Eqs. (A.43) *and* (A.44).

Proof. According to Eq. (A.19), the transformation in Eq. (A.42) from the vessel extents described by Eqs. (A.43) and (A.44) is valid for a CSTR with an ideal mixture, by taking Eqs. (A.20) and (A.21), which results in

$$\mathbf{n}(t) = \left(\mathbf{N}^{\mathrm{T}} - \mathbf{n}_0 \frac{\mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \mathbf{n}_0} \mathbf{N}^{\mathrm{T}}\right) \mathbf{x}_r(t) + \left(\mathbf{W}_{in} - \mathbf{n}_0 \frac{\mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}} \boldsymbol{\rho}^{-1} \mathbf{M}_w \mathbf{n}_0} \mathbf{W}_{in}\right) \mathbf{x}_{in}(t) + \mathbf{n}_0. \tag{A.48}$$

□

Remark A.2. In the case of a homogeneous CSTR with constant density, the transformation in Eq. (A.42) becomes

$$\mathbf{n}(t) = \mathbf{N}^{\mathrm{T}} \mathbf{x}_r(t) + \left(\mathbf{W}_{in} - \frac{\mathbf{n}_0 \mathbf{1}_p^{\mathrm{T}}}{m_0}\right) \mathbf{x}_{in}(t) + \mathbf{n}_0. \tag{A.49}$$

Proposition A.5. *For any open homogeneous reactor with S species, R independent reactions, p independent inlets and one outlet where the inverse of the residence time is the linear combination of reaction rates and inlet flowrates*

$$\omega(t) = \mathbf{k}_r^{\mathrm{T}} \mathbf{r}_v(t) + \mathbf{k}_{in}^{\mathrm{T}} \mathbf{u}_{in}(t), \tag{A.50}$$

the numbers of moles are the linear transformation of R vessel extents of reaction $\mathbf{x}_r(t)$*,* $p-1$ *vessel extents of inlet* $\mathbf{x}_{in}(t)$ *and one vessel extent of initial conditions* $x_{ic}(t)$

$$\mathbf{n}(t) = \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}} \mathbf{k}_r^{\mathrm{T}}\right) \mathbf{x}_r(t) + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}} \mathbf{k}_{in}^{\mathrm{T}}\right) \mathbf{S}_{l,p} \mathbf{x}_{in}(t) + \left(\mathbf{n}_0 - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\right) x_{ic}(t) + \frac{\mathbf{w}_{in,l}}{k_{in,l}}, \tag{A.51}$$

if $l \in \{1, \ldots, p\}$ *is such that* $k_{in,l} \neq 0$*, where* $\mathbf{S}_{l,p}^{\mathrm{T}} = \begin{bmatrix} \mathbf{I}_{l-1} & \mathbf{0}_{l-1} & \mathbf{0}_{(l-1)\times(p-l)} \\ \mathbf{0}_{(p-l)\times(l-1)} & \mathbf{0}_{p-l} & \mathbf{I}_{p-l} \end{bmatrix}$ *is a matrix that selects all but the* l*th element of a* p*-dimensional vector,* $\check{\mathbf{s}}_{l,p}^{\mathrm{T}} = \begin{bmatrix} \mathbf{0}_{l-1}^{\mathrm{T}} & 1 & \mathbf{0}_{p-l}^{\mathrm{T}} \end{bmatrix}$ *is a vector that selects the* l*th element of a* p*-dimensional vector,* $k_{in,l} = \mathbf{k}_{in}^{\mathrm{T}} \check{\mathbf{s}}_{l,p}$*,* $\mathbf{w}_{in,l} = \mathbf{W}_{in} \check{\mathbf{s}}_{l,p}$*, and the vessel extents are described by the ODEs*

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \omega(t) \mathbf{x}_r(t), \qquad \mathbf{x}_r(0) = \mathbf{0}_R, \tag{A.52}$$

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{S}_{l,p}^{\mathrm{T}} \mathbf{u}_{in}(t) - \omega(t) \mathbf{x}_{in}(t), \quad \mathbf{x}_{in}(0) = \mathbf{0}_{p-1}, \tag{A.53}$$

$$\dot{x}_{ic}(t) = -\omega(t) x_{ic}(t), \qquad x_{ic}(0) = 1. \tag{A.54}$$

Proof. Since

$$\mathbf{S}_{l,p} \mathbf{S}_{l,p}^{\mathrm{T}} + \check{\mathbf{s}}_{l,p} \check{\mathbf{s}}_{l,p}^{\mathrm{T}} = \mathbf{I}_p, \tag{A.55}$$

one can observe that

$$\begin{aligned}0 &= \mathbf{k}_r^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{k}_{in}^{\mathrm{T}}\left(\mathbf{S}_{l,p}\mathbf{S}_{l,p}^{\mathrm{T}} + \check{\mathbf{s}}_{l,p}\check{\mathbf{s}}_{l,p}^{\mathrm{T}}\right)\mathbf{u}_{in}(t) - \omega(t)\\ &= \mathbf{k}_r^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{k}_{in}^{\mathrm{T}}\mathbf{S}_{l,p}\mathbf{S}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) + \mathbf{k}_{in}^{\mathrm{T}}\check{\mathbf{s}}_{l,p}\check{\mathbf{s}}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) - \omega(t),\end{aligned} \tag{A.56}$$

which implies that, if $l \in \{1,\ldots,p\}$ is such that $k_{in,l} \neq 0$,

$$\check{\mathbf{s}}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) = \frac{-\mathbf{k}_r^{\mathrm{T}}\mathbf{r}_v(t) - \mathbf{k}_{in}^{\mathrm{T}}\mathbf{S}_{l,p}\mathbf{S}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) + \omega(t)}{k_{in,l}} \tag{A.57}$$

and

$$\begin{aligned}\dot{\mathbf{n}}(t) &= \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}\mathbf{S}_{l,p}\mathbf{S}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) + \mathbf{W}_{in}\check{\mathbf{s}}_{l,p}\check{\mathbf{s}}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}(t)\\ &= \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}\mathbf{S}_{l,p}\mathbf{S}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) + \mathbf{w}_{in,l}\frac{-\mathbf{k}_r^{\mathrm{T}}\mathbf{r}_v(t) - \mathbf{k}_{in}^{\mathrm{T}}\mathbf{S}_{l,p}\mathbf{S}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) + \omega(t)}{k_{in,l}}\\ &\quad - \omega(t)\mathbf{n}(t)\\ &= \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{r}_v(t) + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\mathbf{S}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t)\\ &\quad - \omega(t)\left(\mathbf{n}(t) - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\right).\end{aligned} \tag{A.58}$$

Then, this proposition can be proven by checking the consistency of the initial conditions

$$\begin{aligned}\mathbf{n}(0) &= \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{x}_r(0) + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\mathbf{x}_{in}(0) + \left(\mathbf{n}_0 - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\right)x_{ic}(0)\\ &\quad + \frac{\mathbf{w}_{in,l}}{k_{in,l}}\\ &= \mathbf{n}_0 - \frac{\mathbf{w}_{in,l}}{k_{in,l}} + \frac{\mathbf{w}_{in,l}}{k_{in,l}}\\ &= \mathbf{n}_0,\end{aligned} \tag{A.59}$$

and ODEs

$$\begin{aligned}
\dot{\mathbf{n}}(t) &= \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\dot{\mathbf{x}}_r(t) + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\dot{\mathbf{x}}_{in}(t) + \left(\mathbf{n}_0 - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\right)\dot{x}_{ic}(t) \\
&= \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\left(\mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t)\right) \\
&\quad + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\left(\mathbf{S}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) - \omega(t)\mathbf{x}_{in}(t)\right) \\
&\quad + \left(\mathbf{n}_0 - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\right)\left(-\omega(t)x_{ic}(t)\right) \\
&= \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{r}_v(t) + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\mathbf{S}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) \\
&\quad - \omega(t)\left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{x}_r(t) - \omega(t)\left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\mathbf{x}_{in}(t) \\
&\quad - \omega(t)\left(\mathbf{n}_0 - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\right)x_{ic}(t) \\
&= \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{r}_v(t) + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\mathbf{S}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) \\
&\quad - \omega(t)\left(\mathbf{n}(t) - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\right).
\end{aligned} \tag{A.60}$$

□

Proposition A.6. *For any homogeneous CSTR with S species, R independent reactions and p independent inlets that contains an ideal mixture, the numbers of moles are the linear transformation of R vessel extents of reaction* $\mathbf{x}_r(t)$*,* $p-1$ *vessel extents of inlet* $\mathbf{x}_{in}(t)$ *and one vessel extent of initial conditions* $x_{ic}(t)$

$$\begin{aligned}
\mathbf{n}(t) &= \left(\mathbf{I}_S - \frac{\mathbf{w}_{in,l}\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w\mathbf{w}_{in,l}}\right)\left(\mathbf{N}^{\mathrm{T}}\mathbf{x}_r(t) + \mathbf{W}_{in}\mathbf{S}_{l,p}\mathbf{x}_{in}(t) + \mathbf{n}_0 x_{ic}(t)\right) \\
&\quad + \frac{\mathbf{w}_{in,l}\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w\mathbf{w}_{in,l}}\mathbf{n}_0,
\end{aligned} \tag{A.61}$$

where the vessel extents are described by Eqs. (A.52)*,* (A.53) *and* (A.54)*.*

Proof. According to Eq. (A.19), the transformation in Eq. (A.51) from the vessel extents described by Eqs. (A.52), (A.53) and (A.54) is valid for a CSTR with an ideal mixture, by

taking Eqs. (A.20) and (A.21), which results in

$$\mathbf{n}(t) = \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w\mathbf{w}_{in,l}}\mathbf{N}^{\mathrm{T}}\right)\mathbf{x}_r(t) + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w\mathbf{w}_{in,l}}\mathbf{W}_{in}\right)\mathbf{S}_{l,p}\mathbf{x}_{in}(t) + \left(\mathbf{n}_0 - \frac{\mathbf{w}_{in,l}\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w\mathbf{w}_{in,l}}\mathbf{n}_0\right)x_{ic}(t) + \frac{\mathbf{w}_{in,l}\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w\mathbf{w}_{in,l}}\mathbf{n}_0. \tag{A.62}$$

□

Remark A.3. In the case of a homogeneous CSTR with constant density, since

$$k_{in,l} = \frac{\mathbf{1}_p^{\mathrm{T}}\check{\mathbf{s}}_{l,p}}{m_0} = \frac{1}{m_0}, \tag{A.63}$$

$$\mathbf{k}_{in}^{\mathrm{T}}\mathbf{S}_{l,p} = \frac{\mathbf{1}_p^{\mathrm{T}}\mathbf{S}_{l,p}}{m_0} = \frac{\mathbf{1}_{p-1}^{\mathrm{T}}}{m_0}, \tag{A.64}$$

the transformation in Eq. (A.51) becomes

$$\mathbf{n}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{x}_r(t) + \left(\mathbf{W}_{in}\mathbf{S}_{l,p} - \mathbf{w}_{in,l}\mathbf{1}_{p-1}^{\mathrm{T}}\right)\mathbf{x}_{in}(t) + \left(\mathbf{n}_0 - \mathbf{w}_{in,l}m_0\right)x_{ic}(t) + \mathbf{w}_{in,l}m_0. \tag{A.65}$$

Proposition A.7. *For any open homogeneous reactor with S species, R independent reactions, p independent inlets and one outlet whose numbers of moles are initially at steady state* $\bar{\mathbf{n}}_0$ *and where the inverse of the residence time is the linear combination of reaction rates and inlet flowrates*

$$\omega(t) = \mathbf{k}_r^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{k}_{in}^{\mathrm{T}}\mathbf{u}_{in}(t), \tag{A.66}$$

the numbers of moles are the linear transformation of R vessel extents of reaction $\mathbf{x}_r(t)$ *and* $p-1$ *vessel extents of inlet* $\mathbf{x}_{in}(t)$

$$\mathbf{n}(t) = \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{x}_r(t) + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\mathbf{x}_{in}(t) + \frac{\mathbf{w}_{in,l}}{k_{in,l}}, \tag{A.67}$$

if $l \in \{1,\ldots,p\}$ *is such that* $k_{in,l} \neq 0$*, where* $\mathbf{S}_{l,p}^{\mathrm{T}} = \begin{bmatrix} \mathbf{I}_{l-1} & \mathbf{0}_{l-1} & \mathbf{0}_{(l-1)\times(p-l)} \\ \mathbf{0}_{(p-l)\times(l-1)} & \mathbf{0}_{p-l} & \mathbf{I}_{p-l} \end{bmatrix}$ *is a matrix that selects all but the* l*th element of a* p*-dimensional vector,* $\check{\mathbf{s}}_{l,p}^{\mathrm{T}} = \begin{bmatrix} \mathbf{0}_{l-1}^{\mathrm{T}} & 1 & \mathbf{0}_{p-l}^{\mathrm{T}} \end{bmatrix}$ *is a vector that selects the* l*th element of a* p*-dimensional vector,* $k_{in,l} = \mathbf{k}_{in}^{\mathrm{T}}\check{\mathbf{s}}_{l,p}$*,* $\mathbf{w}_{in,l} = \mathbf{W}_{in}\check{\mathbf{s}}_{l,p}$*, and the vessel extents are described by the ODEs*

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t), \qquad \mathbf{x}_r(0) = \frac{\bar{\mathbf{r}}_v}{\bar{\omega}}, \tag{A.68}$$

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{S}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) - \omega(t)\mathbf{x}_{in}(t), \quad \mathbf{x}_{in}(0) = \frac{\mathbf{S}_{l,p}^{\mathrm{T}}\bar{\mathbf{u}}_{in}}{\bar{\omega}}, \tag{A.69}$$

with $\bar{\mathbf{r}}_v$, $\bar{\mathbf{u}}_{in}$ *and* $\bar{\omega}$ *the reaction rates, inlet flowrates and inverse of the residence time at steady state.*

Proof. As shown before, if $l \in \{1, \ldots, p\}$ is such that $k_{in,l} \neq 0$,

$$\begin{aligned}\dot{\mathbf{n}}(t) = &\left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{r}_v(t) + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\mathbf{S}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) \\ &- \omega(t)\left(\mathbf{n}(t) - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\right).\end{aligned} \tag{A.70}$$

Now, let us note that, at steady state,

$$\mathbf{0}_S = \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\bar{\mathbf{r}}_v + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\mathbf{S}_{l,p}^{\mathrm{T}}\bar{\mathbf{u}}_{in} - \bar{\omega}\left(\bar{\mathbf{n}}_0 - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\right), \tag{A.71}$$

which implies that

$$\bar{\mathbf{n}}_0 = \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\frac{\bar{\mathbf{r}}_v}{\bar{\omega}} + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\frac{\mathbf{S}_{l,p}^{\mathrm{T}}\bar{\mathbf{u}}_{in}}{\bar{\omega}} + \frac{\mathbf{w}_{in,l}}{k_{in,l}}. \tag{A.72}$$

Then, this proposition can be proven by checking the consistency of the initial conditions

$$\begin{aligned}\mathbf{n}(0) &= \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{x}_r(0) + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\mathbf{x}_{in}(0) + \frac{\mathbf{w}_{in,l}}{k_{in,l}} \\ &= \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\frac{\bar{\mathbf{r}}_v}{\bar{\omega}} + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\frac{\mathbf{S}_{l,p}^{\mathrm{T}}\bar{\mathbf{u}}_{in}}{\bar{\omega}} + \frac{\mathbf{w}_{in,l}}{k_{in,l}} \\ &= \bar{\mathbf{n}}_0,\end{aligned} \tag{A.73}$$

and ODEs

$$\begin{aligned}
\dot{\mathbf{n}}(t) &= \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\dot{\mathbf{x}}_r(t) + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\dot{\mathbf{x}}_{in}(t) \\
&= \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\left(\mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t)\right) \\
&\quad + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\left(\mathbf{S}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) - \omega(t)\mathbf{x}_{in}(t)\right) \\
&= \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{r}_v(t) + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\mathbf{S}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) \\
&\quad - \omega(t)\left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{x}_r(t) - \omega(t)\left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\mathbf{x}_{in}(t) \\
&= \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_r^{\mathrm{T}}\right)\mathbf{r}_v(t) + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\mathbf{k}_{in}^{\mathrm{T}}\right)\mathbf{S}_{l,p}\mathbf{S}_{l,p}^{\mathrm{T}}\mathbf{u}_{in}(t) \\
&\quad - \omega(t)\left(\mathbf{n}(t) - \frac{\mathbf{w}_{in,l}}{k_{in,l}}\right).
\end{aligned} \tag{A.74}$$

□

Proposition A.8. *For any homogeneous CSTR with S species, R independent reactions and p independent inlets whose numbers of moles are initially at steady state* $\tilde{\mathbf{n}}_0$ *and that contains an ideal mixture, the numbers of moles are the linear transformation of R vessel extents of reaction* $\mathbf{x}_r(t)$ *and* $p-1$ *vessel extents of inlet* $\mathbf{x}_{in}(t)$

$$\mathbf{n}(t) = \left(\mathbf{I}_S - \frac{\mathbf{w}_{in,l}\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w\mathbf{w}_{in,l}}\right)\left(\mathbf{N}^{\mathrm{T}}\mathbf{x}_r(t) + \mathbf{W}_{in}\mathbf{S}_{l,p}\mathbf{x}_{in}(t)\right) + \frac{\mathbf{w}_{in,l}\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w\mathbf{w}_{in,l}}\mathbf{n}_0, \tag{A.75}$$

where the vessel extents are described by Eqs. (A.68) *and* (A.69).

Proof. According to Eq. (A.19), the transformation in Eq. (A.67) from the vessel extents described by Eqs. (A.68) and (A.69) is valid for a CSTR with an ideal mixture, by taking Eqs. (A.20) and (A.21), which results in

$$\begin{aligned}
\mathbf{n}(t) &= \left(\mathbf{N}^{\mathrm{T}} - \frac{\mathbf{w}_{in,l}\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w\mathbf{w}_{in,l}}\mathbf{N}^{\mathrm{T}}\right)\mathbf{x}_r(t) + \left(\mathbf{W}_{in} - \frac{\mathbf{w}_{in,l}\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w\mathbf{w}_{in,l}}\mathbf{W}_{in}\right)\mathbf{S}_{l,p}\mathbf{x}_{in}(t) \\
&\quad + \frac{\mathbf{w}_{in,l}\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w}{\mathbf{1}_S^{\mathrm{T}}\boldsymbol{\rho}^{-1}\mathbf{M}_w\mathbf{w}_{in,l}}\mathbf{n}_0.
\end{aligned} \tag{A.76}$$

□

Remark A.4. In the case of a homogeneous CSTR with constant density, since

$$k_{in,l} = \frac{\mathbf{1}_p^{\mathrm{T}} \check{\mathbf{s}}_{l,p}}{m_0} = \frac{1}{m_0}, \tag{A.77}$$

$$\mathbf{k}_{in}^{\mathrm{T}} \mathbf{S}_{l,p} = \frac{\mathbf{1}_p^{\mathrm{T}} \mathbf{S}_{l,p}}{m_0} = \frac{\mathbf{1}_{p-1}^{\mathrm{T}}}{m_0}, \tag{A.78}$$

the transformation in Eq. (A.67) becomes

$$\mathbf{n}(t) = \mathbf{N}^{\mathrm{T}} \mathbf{x}_r(t) + \left(\mathbf{W}_{in} \mathbf{S}_{l,p} - \mathbf{w}_{in,l} \mathbf{1}_{p-1}^{\mathrm{T}} \right) \mathbf{x}_{in}(t) + \mathbf{w}_{in,l} m_0. \tag{A.79}$$

A.4 Combined Material and Heat Balance Equations

A.4.1 Homogeneous reaction systems

The vessel extent of heat exchange $x_{ex}(t)$ represents the amount of energy that has transferred via heat exchange and is in the vessel at time t, that is, discounting for the amount that has left the vessel via the outlet. This vessel extent is described by the ODE

$$\dot{x}_{ex}(t) = q_{ex}(t) - \omega(t) x_{ex}(t), \qquad x_{ex}(0) = 0. \tag{A.80}$$

Let us assume that the inlet composition given by $\mathbf{W}_{in}(t)$ and the inlet composition and temperature given by $\check{\mathbf{T}}_{in}(t)$ are constant. Eqs. (2.19) and (2.44) can be reconstructed from Eqs. (2.95), (2.99), (2.103) and (A.80) using

$$\mathbf{z}(t) = \mathscr{L} \begin{bmatrix} \mathbf{x}_r(t) \\ x_{ex}(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \end{bmatrix}, \tag{A.81}$$

with $\mathscr{L} = \begin{bmatrix} \mathbf{N}^{\mathrm{T}} & 0 & \mathbf{W}_{in} & \mathbf{n}_0 \\ -\Delta \mathbf{H}_r^{\mathrm{T}} & 1 & \check{\mathbf{T}}_{in}^{\mathrm{T}} & Q_0 \end{bmatrix}$.

If $\mathrm{rank}(\mathscr{L}) = R + p + 2$, the vessel extents are given by the linear transformation

$$\begin{bmatrix} \mathbf{x}_r(t) \\ x_{ex}(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \end{bmatrix} = \mathscr{T} \mathbf{z}(t), \tag{A.82}$$

with $\mathscr{T} := \left(\mathscr{L}^{\mathrm{T}} \mathbf{W} \mathscr{L} \right)^{-1} \mathscr{L}^{\mathrm{T}} \mathbf{W}$.

The null space of $\mathscr{L}^{\mathrm{T}}$ is of dimension $q := S + 1 - \mathrm{rank}(\mathscr{L})$ and is described by the

$(S+1)\times q$ matrix $\mathbf{P}$. Then, the q invariants $\mathbf{x}_{iv}(t) = \mathbf{0}_q$ are given by the linear transformation

$$\mathbf{x}_{iv}(t) = \mathbf{P}^{\mathrm{T}}\mathbf{z}(t). \tag{A.83}$$

A.4.2 Reaction systems with instantaneous equilibria

Let us assume that the inlet composition given by $\mathbf{W}_{in}(t)$ and the inlet composition and temperature given by $\check{\mathbf{T}}_{in}(t)$ are constant. Eqs. (2.56) and (2.62) can be reconstructed from Eqs. (2.99), (2.103), (2.134) and (A.80) using

$$\mathbf{z}_s(t) = \mathscr{L}_s \begin{bmatrix} \mathbf{x}_{r,s}(t) \\ x_{ex}(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \end{bmatrix}, \tag{A.84}$$

with $\mathscr{L}_s = \begin{bmatrix} \mathbf{P}_e^{\mathrm{T}} & \mathbf{0}_{S_s} \\ \Delta\mathbf{H}_e^{\mathrm{T}} & 1 \end{bmatrix} \begin{bmatrix} \mathbf{N}_s^{\mathrm{T}} & 0 & \mathbf{W}_{in} & \mathbf{n}_0 \\ -\Delta\mathbf{H}_{r,s}^{\mathrm{T}} & 1 & \check{\mathbf{T}}_{in}^{\mathrm{T}} & Q_0 \end{bmatrix}$.

If $\operatorname{rank}(\mathscr{L}_s) = R_s + p + 2$, the vessel extents are given by the linear transformation

$$\begin{bmatrix} \mathbf{x}_{r,s}(t) \\ x_{ex}(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \end{bmatrix} = \mathscr{T}_s \mathbf{z}_s(t), \tag{A.85}$$

with $\mathscr{T}_s := \left(\mathscr{L}_s^{\mathrm{T}}\mathbf{W}\mathscr{L}_s\right)^{-1}\mathscr{L}_s^{\mathrm{T}}\mathbf{W}$.

The null space of $\mathscr{L}_s^{\mathrm{T}}$ is of dimension $q_s := S_s + 1 - \operatorname{rank}(\mathscr{L}_s)$ and is described by the $(S_s+1)\times q_s$ matrix $\mathbf{P}_s$. Then, the q_s invariants $\mathbf{x}_{iv,s}(t) = \mathbf{0}_{q_s}$ are given by the linear transformation

$$\mathbf{x}_{iv,s}(t) = \mathbf{P}_s^{\mathrm{T}}\mathbf{z}_s(t). \tag{A.86}$$

A.4.3 Multiphase reaction systems

The vessel extent of heat exchange $x_{ex,f}(t)$ represents the amount of energy that has transferred to phase F via heat exchange and is in the vessel at time t, that is, discounting for the amount that has left the vessel via the outlet. This vessel extent is described by the ODE

$$\dot{x}_{ex,f}(t) = q_{ex,f}(t) - \omega_f(t)x_{ex,f}(t), \qquad x_{ex,f}(0) = 0. \tag{A.87}$$

Let us assume that the inlet composition given by $\mathbf{W}_{in,f}(t)$ and the inlet composition and temperature given by $\check{\mathbf{T}}_{in,f}(t)$ are constant. Eqs. (2.63) and (2.66) can be reconstructed

from Eqs. (2.138), (2.139), (2.140), (2.141) and (A.87) using

$$\mathbf{z}_f(t) = \mathscr{L}_f \begin{bmatrix} \mathbf{x}_{r,f}(t) \\ \mathbf{x}_{m,f}(t) \\ x_{ex,f}(t) \\ \mathbf{x}_{in,f}(t) \\ x_{ic,f}(t) \end{bmatrix}, \tag{A.88}$$

with $\mathscr{L}_f = \begin{bmatrix} \mathbf{N}_f^{\mathrm{T}} & \mathbf{E}_{m,f} & 0 & \mathbf{W}_{in,f} & \mathbf{n}_{f,0} \\ -\Delta\mathbf{H}_{r,f}^{\mathrm{T}} & -\Delta\mathbf{H}_{m,f}^{\mathrm{T}} & 1 & \check{\mathbf{T}}_{in,f}^{\mathrm{T}} & Q_{f,0} \end{bmatrix}$.

If $\operatorname{rank}\left(\mathscr{L}_f\right) = R_f + p_{m,f} + p_f + 2$, the vessel extents are given by the linear transformation

$$\begin{bmatrix} \mathbf{x}_{r,f}(t) \\ \mathbf{x}_{m,f}(t) \\ x_{ex,f}(t) \\ \mathbf{x}_{in,f}(t) \\ x_{ic,f}(t) \end{bmatrix} = \mathscr{T}_f \mathbf{z}_f(t), \tag{A.89}$$

with $\mathscr{T}_f := \left(\mathscr{L}_f^{\mathrm{T}} \mathbf{W} \mathscr{L}_f\right)^{-1} \mathscr{L}_f^{\mathrm{T}} \mathbf{W}$.

The null space of $\mathscr{L}_f^{\mathrm{T}}$ is of dimension $q_f := S_f + 1 - \operatorname{rank}\left(\mathscr{L}_f\right)$ and is described by the $(S_f + 1) \times q_f$ matrix $\mathbf{P}_f$. Then, the q_f invariants $\mathbf{x}_{iv,f}(t) = \mathbf{0}_{q_f}$ are given by the linear transformation

$$\mathbf{x}_{iv,f}(t) = \mathbf{P}_f^{\mathrm{T}} \mathbf{z}_f(t). \tag{A.90}$$

B Appendix of Chapter 3

B.1 Combined Material and Heat Balance Equations

B.1.1 Single-phase lumped reactors

The heat $Q(t)$ is described by the ODE

$$\frac{\mathrm{d}}{\mathrm{d}t}Q + \omega Q = \left(-\mathbf{\Delta H}_r^{\mathrm{T}}\right)\mathbf{r}_v + \check{\mathbf{T}}_{in}^{\mathrm{T}}\mathbf{u}_{in}, \quad Q(0) = Q_0, \tag{B.1}$$

where $Q(t) := \bar{\mathbf{c}}_p(t)^{\mathrm{T}}\mathbf{n}(t)\left(T(t) - T_{ref}\right)$, with $T(t)$ the temperature and the S-dimensional vector of average molar heat capacities $\bar{\mathbf{c}}_p(t) := \int_{T_{ref}}^{T(t)} \mathbf{c}_p(\theta)\mathrm{d}\theta / \left(T(t) - T_{ref}\right)$ between $T(t)$ and T_{ref}, $\mathbf{\Delta H}_r := \mathbf{N}\mathbf{\Delta H}$ is the R-dimensional vector of enthalpies of reaction, with $\mathbf{\Delta H}$ the S-dimensional vector of enthalpies of formation at temperature T_{ref}, and $\check{\mathbf{T}}_{in}(t)$ is a p-dimensional vector, whose jth element is the specific heat of the jth inlet $\check{T}_{in,j}(t) := \bar{\mathbf{c}}_{p,in,j}(t)^{\mathrm{T}}\mathbf{W}_{in,j}(t)\left(T_{in,j}(t) - T_{ref}\right)$ at temperature $T_{in,j}(t)$, with the S-dimensional vector of average molar heat capacities $\bar{\mathbf{c}}_{p,in,j}(t) := \int_{T_{ref}}^{T_{in,j}(t)} \mathbf{c}_p(\theta)\,\mathrm{d}\theta / \left(T_{in,j}(t) - T_{ref}\right)$ between $T_{in,j}(t)$ and T_{ref}.

Let us define $\mathbf{z} := \left[\begin{smallmatrix}\mathbf{n}\\ Q\end{smallmatrix}\right]$. The effect of the outlet flow on the initial and inlet flow conditions can be computed as $\mathbf{z}_{iic}(t) := \left[\begin{smallmatrix}\mathbf{n}_{iic}(t)\\ Q_{iic}(t)\end{smallmatrix}\right]$ by solving the ODE

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{z}_{iic} + \omega\,\mathbf{z}_{iic} = \begin{bmatrix}\mathbf{W}_{in}\\ \check{\mathbf{T}}_{in}^{\mathrm{T}}\end{bmatrix}\mathbf{u}_{in}, \quad \mathbf{z}_{iic}(0) = \begin{bmatrix}\mathbf{n}_0\\ Q_0\end{bmatrix}. \tag{B.2}$$

Eqs. (3.1) and (B.1) can be reconstructed using

$$\mathbf{z} = \mathscr{L}\,\mathbf{x}_r + \mathbf{z}_{iic}, \tag{B.3}$$

with $\mathscr{L} = \left[\begin{smallmatrix}\mathbf{N}^{\mathrm{T}}\\ -\mathbf{\Delta H}_r^{\mathrm{T}}\end{smallmatrix}\right]$. If $\mathrm{rank}(\mathscr{L}) = R$, the vessel extents of reaction are given by the linear transformation in Eq. (3.5), replacing $\delta\mathbf{n}$ by $\delta\mathbf{z} := \mathbf{z} - \mathbf{z}_{iic}$.

B.1.2 Single-phase plug-flow reactors

The volumetric heat $h(z,t)$ is described by the PDE

$$\frac{\partial}{\partial t}h + \frac{\partial}{\partial z}\left(v_z h\right) = \left(-\boldsymbol{\Delta}\mathbf{H}_r^{\mathrm{T}}\right)\mathbf{r}, \tag{B.4}$$

where $h(z,t) := \bar{\mathbf{c}}_p(z,t)^{\mathrm{T}}\mathbf{c}(z,t)\left(T(z,t) - T_{ref}\right)$, with the average molar heat capacities $\bar{\mathbf{c}}_p(z,t) := \int_{T_{ref}}^{T(z,t)} \mathbf{c}_p(\theta)\,\mathrm{d}\theta / \left(T(z,t) - T_{ref}\right)$.

Eq. (B.4) is subject to the following initial and advective boundary conditions:

$$h(z,0) = h_0(z), \quad \forall z > 0 \quad \text{(IC)},$$
$$h(0,t) = h_{in}(t), \quad \forall t \geq 0 \quad \text{(BC)}.$$

Let us define $\mathbf{z} := \left[\begin{smallmatrix}\mathbf{c}\\ h\end{smallmatrix}\right]$. The effect of advection on the initial and advective boundary conditions can be computed as $\mathbf{z}_{ibc}(z,t) := \left[\begin{smallmatrix}\mathbf{c}_{ibc}(z,t)\\ h_{ibc}(z,t)\end{smallmatrix}\right]$ by solving the PDE

$$\frac{\partial}{\partial t}\mathbf{z}_{ibc} + \frac{\partial}{\partial z}\left(v_z \mathbf{z}_{ibc}\right) = \mathbf{0}_{S+1}, \tag{B.5}$$

with the initial and boundary conditions

$$\mathbf{z}_{ibc}(z,0) = \begin{bmatrix}\mathbf{c}_0(z)\\ h_0(z)\end{bmatrix}, \quad \forall z > 0 \quad \text{(IC)}, \tag{B.6}$$
$$\mathbf{z}_{ibc}(0,t) = \begin{bmatrix}\mathbf{c}_{in}(t)\\ h_{in}(t)\end{bmatrix}, \quad \forall t \geq 0 \quad \text{(BC)}. \tag{B.7}$$

Eqs. (3.6) and (B.4) can be reconstructed using

$$\mathbf{z} = \mathscr{L}\,\mathbf{x}_r + \mathbf{z}_{ibc}, \tag{B.8}$$

with $\mathscr{L} = \left[\begin{smallmatrix}\mathbf{N}^{\mathrm{T}}\\ -\boldsymbol{\Delta}\mathbf{H}_r^{\mathrm{T}}\end{smallmatrix}\right]$. If $\mathrm{rank}(\mathscr{L}) = R$, the extents of reaction are given by the linear transformation in Eq. (3.12), replacing $\delta\mathbf{c}$ by $\delta\mathbf{z} := \mathbf{z} - \mathbf{z}_{ibc}$.

B.1.3 Single-phase one-dimensional tubular reactors

The volumetric heat $h(z,t)$ is described by the PDE

$$\frac{\partial}{\partial t}h + \frac{\partial}{\partial z}\left(v_z h\right) = \left(-\boldsymbol{\Delta}\mathbf{H}_r^{\mathrm{T}}\right)\mathbf{r} + \left(-\boldsymbol{\Delta}\mathbf{H}_d^{\mathrm{T}}\right)\boldsymbol{\phi}_d + \phi_c + \phi_{ex}, \tag{B.9}$$

where $\boldsymbol{\Delta}\mathbf{H}_d := \mathbf{E}_d^{\mathrm{T}}\boldsymbol{\Delta}\mathbf{H}$ is the p_d-dimensional vector of enthalpies of diffusion, ϕ_c is the rate of heat conduction, and ϕ_{ex} is the rate of heat exchange from external sources.

Diffusion is described by Eq. (3.14), with the corresponding boundary conditions, while heat conduction calls for the definition of the heat conduction flux in the z-direction, de-

noted $j_{c,z}(z,t)$, which is described by the PDE

$$\frac{\partial}{\partial z} j_{c,z} = -\phi_c, \tag{B.10}$$

with the conductive boundary conditions

$$\lim_{z\to\infty} j_{c,z}(z,t) = 0, \ \forall t \geq 0.$$

Eq. (B.9) is subject to the following initial and advective boundary conditions:

$$\begin{aligned} &h(z,0) = h_0(z), && \forall z > 0 \quad \text{(IC)}, \\ &h(0,t) = h_{in}(t) + h_d(t) + h_c(t), && \forall t \geq 0 \quad \text{(BC)}, \end{aligned}$$

with $h_d(t) := -\frac{\left(-\boldsymbol{\Delta}\mathbf{H}_d^{\mathrm{T}}\right)\mathbf{j}_{d,z}(0,t)}{\beta v_z(0,t)}$ and $h_c(t) := -\frac{j_{c,z}(0,t)}{\beta v_z(0,t)}$. These initial and boundary conditions are also affected by those of Eqs. (3.14) and (B.10).

Let us define $\mathbf{z} := \left[\begin{smallmatrix} \mathbf{c} \\ h \end{smallmatrix}\right]$. The effect of advection on the initial and advective boundary conditions can be computed by solving Eq. (B.5), with the initial and boundary conditions given by Eqs. (B.6) and (B.7).

Extent of heat conduction The extent of heat conduction $x_c(z,t)$ represents the amount of energy that has transferred via heat conduction and is at position z at time t. This extent is described by the PDE

$$\frac{\partial}{\partial t} x_c + \frac{\partial}{\partial z}\left(v_z x_c\right) = \phi_c, \tag{B.11}$$

with $x_c(z,0) = 0, \forall z > 0$ (IC) and $x_c(0,t) = h_c(t), \forall t \geq 0$ (BC).

Extent of heat exchange The extent of heat exchange $x_{ex}(z,t)$ represents the amount of energy that has transferred via heat exchange and is at position z at time t. This extent is described by the PDE

$$\frac{\partial}{\partial t} x_{ex} + \frac{\partial}{\partial z}\left(v_z x_{ex}\right) = \phi_{ex}, \tag{B.12}$$

with $x_{ex}(z,0) = 0, \forall z > 0$ (IC) and $x_{ex}(0,t) = 0, \forall t \geq 0$ (BC).

Eqs. (3.13) and (B.9) can be reconstructed using

$$\mathbf{z} = \mathscr{L}\begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_d \\ x_c + x_{ex} \end{bmatrix} + \mathbf{z}_{ibc}, \tag{B.13}$$

with $\mathscr{L} = \begin{bmatrix} \mathbf{N}^{\mathrm{T}} & \mathbf{E}_d & \mathbf{0}_S \\ -\boldsymbol{\Delta}\mathbf{H}_r^{\mathrm{T}} & -\boldsymbol{\Delta}\mathbf{H}_d^{\mathrm{T}} & 1 \end{bmatrix}$. If $\operatorname{rank}(\mathscr{L}) = R + p_d + 1$, the extents are given by the linear

transformation

$$\begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_d \\ x_c + x_{ex} \end{bmatrix} = \mathscr{T}\,\delta\mathbf{z}, \tag{B.14}$$

with $\mathscr{T} := \left(\mathscr{L}^{\mathrm{T}}\mathbf{W}\mathscr{L}\right)^{-1}\mathscr{L}^{\mathrm{T}}\mathbf{W}$, and $\delta\mathbf{z} := \mathbf{z} - \mathbf{z}_{ibc}$.

B.1.4 Multiphase one-dimensional tubular reactors

The volumetric heat $h_f^\varepsilon(z,t)$ is described by the PDE

$$\begin{aligned}\frac{\partial}{\partial t}h_f^\varepsilon + \frac{\partial}{\partial z}\left(v_{f,z}h_f^\varepsilon\right) = &\left(-\boldsymbol{\Delta}\mathbf{H}_{r,f}^{\mathrm{T}}\right)\mathbf{r}_f^\varepsilon + \left(-\boldsymbol{\Delta}\mathbf{H}_{m,f}^{\mathrm{T}}\right)\boldsymbol{\phi}_{m,f}^\varepsilon \\ &+ \left(-\boldsymbol{\Delta}\mathbf{H}_{d,f}^{\mathrm{T}}\right)\boldsymbol{\phi}_{d,f}^\varepsilon + \phi_{c,f}^\varepsilon + \phi_{ex,f}^\varepsilon,\end{aligned} \tag{B.15}$$

where $\boldsymbol{\Delta}\mathbf{H}_{m,f} := \mathbf{E}_{m,f}^{\mathrm{T}}\boldsymbol{\Delta}\mathbf{H}_f$ is the $p_{m,f}$-dimensional vector of enthalpies of mass transfer to phase F.

Diffusion is described by Eq. (3.19), with the corresponding boundary conditions, while the heat conduction flux in the z-direction, denoted $j_{c,f,z}^\varepsilon(z,t)$, is described by the PDE

$$\frac{\partial}{\partial z}j_{c,f,z}^\varepsilon = -\phi_{c,f}^\varepsilon, \tag{B.16}$$

with the conductive boundary conditions

$$\lim_{z\to\infty} j_{c,f,z}^\varepsilon(z,t) = 0,\ \forall t \geq 0.$$

Eq. (B.15) is subject to the following initial and advective boundary conditions:

$$\begin{aligned} &h_f^\varepsilon(z,0) = h_{f,0}^\varepsilon(z), && \forall z > 0 \quad \text{(IC)}, \\ &h_f^\varepsilon(0,t) = h_{f,in}^\varepsilon(t) + h_{d,f}^\varepsilon(t) + h_{c,f}^\varepsilon(t), && \forall t \geq 0 \quad \text{(BC)}, \end{aligned}$$

with $h_{d,f}^\varepsilon(t) := -\frac{\left(-\boldsymbol{\Delta}\mathbf{H}_{d,f}^{\mathrm{T}}\right)\mathbf{j}_{d,f,z}^\varepsilon(0,t)}{\beta v_{f,z}(0,t)}$, and $h_{c,f}^\varepsilon(t) := -\frac{j_{c,f,z}^\varepsilon(0,t)}{\beta v_{f,z}(0,t)}$.

Let us define $\mathbf{z}_f^\varepsilon := \begin{bmatrix} \mathbf{c}_f^\varepsilon \\ h_f^\varepsilon \end{bmatrix}$. The effect of advection on the initial and advective boundary conditions can be computed as $\mathbf{z}_{ibc,f}^\varepsilon(z,t) := \begin{bmatrix} \mathbf{c}_{ibc,f}^\varepsilon(z,t) \\ h_{ibc,f}^\varepsilon(z,t) \end{bmatrix}$ by solving the PDE

$$\frac{\partial}{\partial t}\mathbf{z}_{ibc,f}^\varepsilon + \frac{\partial}{\partial z}\left(v_{f,z}\mathbf{z}_{ibc,f}^\varepsilon\right) = \mathbf{0}_{S_f+1}, \tag{B.17}$$

with the initial and boundary conditions

$$\mathbf{z}^{\varepsilon}_{ibc,f}(z,0) = \begin{bmatrix} \mathbf{c}^{\varepsilon}_{f,0}(z) \\ h^{\varepsilon}_{f,0}(z) \end{bmatrix}, \quad \forall z > 0 \quad \text{(IC)}, \tag{B.18}$$

$$\mathbf{z}^{\varepsilon}_{ibc,f}(0,t) = \begin{bmatrix} \mathbf{c}^{\varepsilon}_{f,in}(t) \\ h^{\varepsilon}_{f,in}(t) \end{bmatrix}, \quad \forall t \geq 0 \quad \text{(BC)}. \tag{B.19}$$

Extent of heat conduction The extent of heat conduction $x_{c,f}(z,t)$ represents the amount of energy that has transferred via heat conduction in phase F and is at position z at time t. This extent is described by the PDE

$$\frac{\partial}{\partial t} x_{c,f} + \frac{\partial}{\partial z}\left(v_{f,z} x_{c,f}\right) = \phi^{\varepsilon}_{c,f}, \tag{B.20}$$

with $x_{c,f}(z,0) = 0, \forall z > 0$ (IC) and $x_{c,f}(0,t) = h^{\varepsilon}_{c,f}(t), \forall t \geq 0$ (BC).

Extent of heat exchange The extent of heat exchange $x_{ex,f}(z,t)$ represents the amount of energy that has transferred to phase F via heat exchange and is at position z at time t. This extent is described by the PDE

$$\frac{\partial}{\partial t} x_{ex,f} + \frac{\partial}{\partial z}\left(v_{f,z} x_{ex,f}\right) = \phi^{\varepsilon}_{ex,f}, \tag{B.21}$$

with $x_{ex,f}(z,0) = 0, \forall z > 0$ (IC) and $x_{ex,f}(0,t) = 0, \forall t \geq 0$ (BC).

Eqs. (3.18) and (B.15) can be reconstructed using

$$\mathbf{z}^{\varepsilon}_{f} = \mathscr{L}_f \begin{bmatrix} \mathbf{x}_{r,f} \\ \mathbf{x}_{m,f} \\ \mathbf{x}_{d,f} \\ x_{c,f} + x_{ex,f} \end{bmatrix} + \mathbf{z}^{\varepsilon}_{ibc,f}, \tag{B.22}$$

with $\mathscr{L}_f = \begin{bmatrix} \mathbf{N}_f^{\mathrm{T}} & \mathbf{E}_{m,f} & \mathbf{E}_{d,f} & \mathbf{0}_{S_f} \\ -\boldsymbol{\Delta}\mathbf{H}_{r,f}^{\mathrm{T}} & -\boldsymbol{\Delta}\mathbf{H}_{m,f}^{\mathrm{T}} & -\boldsymbol{\Delta}\mathbf{H}_{d,f}^{\mathrm{T}} & 1 \end{bmatrix}$. If $\operatorname{rank}\left(\mathscr{L}_f\right) = R_f + p_{m,f} + p_{d,f} + 1$, the extents are given by the linear transformation

$$\begin{bmatrix} \mathbf{x}_{r,f} \\ \mathbf{x}_{m,f} \\ \mathbf{x}_{d,f} \\ x_{c,f} + x_{ex,f} \end{bmatrix} = \mathscr{T}_f \, \delta\mathbf{z}^{\varepsilon}_{f}, \tag{B.23}$$

with $\mathscr{T}_f := \left(\mathscr{L}_f^{\mathrm{T}} \mathbf{W} \mathscr{L}_f\right)^{-1} \mathscr{L}_f^{\mathrm{T}} \mathbf{W}$, and $\delta\mathbf{z}^{\varepsilon}_{f} := \mathbf{z}^{\varepsilon}_{f} - \mathbf{z}^{\varepsilon}_{ibc,f}$.

B.1.5 Multiphase two-dimensional tubular reactors

The volumetric heat $h^{\varepsilon}_{f}(z,r,t)$ is described by the PDE in Eq. (B.15).

Diffusion is described by Eq. (3.28), with the corresponding boundary conditions, while the heat conduction fluxes in the radial direction r and axial direction, denoted $j^{\varepsilon}_{c,f,r}(z,r,t)$

and $j^{\varepsilon}_{c,f,z}(z,r,t)$, are described by the PDE

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\, j^{\varepsilon}_{c,f,r}\right)+\frac{\partial}{\partial z} j^{\varepsilon}_{c,f,z}=-\phi^{\varepsilon}_{c,f}, \tag{B.24}$$

with the conductive boundary conditions

$$\begin{aligned} j^{\varepsilon}_{c,f,r}(z,0,t)&=0, \quad \forall z\geq 0, \qquad \forall t\geq 0,\\ j^{\varepsilon}_{c,f,r}(z,\mathscr{R},t)&=0, \quad \forall z\geq 0, \qquad \forall t\geq 0,\\ \lim_{z\to\infty} j^{\varepsilon}_{c,f,z}(z,r,t)&=0,\ \forall r\in\,]0,\mathscr{R}[,\ \forall t\geq 0. \end{aligned}$$

Eq. (B.15) is subject to the following initial and advective boundary conditions:

$$\begin{aligned} h^{\varepsilon}_{f}(z,r,0)&=h^{\varepsilon}_{f,0}(z,r), \quad \forall z>0,\ \forall r\in\,]0,\mathscr{R}[\qquad \text{(IC)},\\ h^{\varepsilon}_{f}(0,r,t)&=h^{\varepsilon}_{f,in}(r,t)+h^{\varepsilon}_{d,f}(r,t)+h^{\varepsilon}_{c,f}(r,t),\\ &\qquad\qquad \forall r\in\,]0,\mathscr{R}[,\ \forall t\geq 0 \qquad \text{(BC)}, \end{aligned}$$

with $h^{\varepsilon}_{d,f}(r,t):=-\frac{\left(-\mathbf{\Delta H}^{\mathrm{T}}_{d,f}\right)\mathbf{j}^{\varepsilon}_{d,f,z}(0,r,t)}{\beta\nu_{f,z}(0,r,t)}$ and $h^{\varepsilon}_{c,f}(r,t):=-\frac{j^{\varepsilon}_{c,f,z}(0,r,t)}{\beta\nu_{f,z}(0,r,t)}$.

Let us define $\mathbf{z}^{\varepsilon}_{f}:=\begin{bmatrix}\mathbf{c}^{\varepsilon}_{f}\\ h^{\varepsilon}_{f}\end{bmatrix}$. The effect of advection on the initial and advective boundary conditions can be computed as $\mathbf{z}^{\varepsilon}_{ibc,f}(z,r,t):=\begin{bmatrix}\mathbf{c}^{\varepsilon}_{ibc,f}(z,r,t)\\ h^{\varepsilon}_{ibc,f}(z,r,t)\end{bmatrix}$ by solving Eq. (B.17) with the initial and boundary conditions

$$\begin{aligned} \mathbf{z}^{\varepsilon}_{ibc,f}(z,r,0)&=\begin{bmatrix}\mathbf{c}^{\varepsilon}_{f,0}(z,r)\\ h^{\varepsilon}_{f,0}(z,r)\end{bmatrix}, \quad \forall z>0,\ \forall r\in\,]0,\mathscr{R}[\quad \text{(IC)},\\ \mathbf{z}^{\varepsilon}_{ibc,f}(0,r,t)&=\begin{bmatrix}\mathbf{c}^{\varepsilon}_{f,in}(r,t)\\ h^{\varepsilon}_{f,in}(r,t)\end{bmatrix}, \quad \forall r\in\,]0,\mathscr{R}[,\ \forall t\geq 0 \quad \text{(BC)}. \end{aligned}$$

Extent of heat conduction The extent of heat conduction $x_{c,f}(z,r,t)$ is computed using Eq. (B.20), with $x_{c,f}(z,r,0)=0,\ \forall z>0,\ \forall r\in\,]0,\mathscr{R}[$ (IC) and $x_{c,f}(0,r,t)=h^{\varepsilon}_{c,f}(r,t)$, $\forall r\in\,]0,\mathscr{R}[,\ \forall t\geq 0$ (BC).

Extent of heat exchange The extent of heat exchange $x_{ex,f}(z,r,t)$ is computed using Eq. (B.21), with $x_{ex,f}(z,r,0)=0,\ \forall z>0,\ \forall r\in\,]0,\mathscr{R}[$ (IC) and $x_{ex,f}(0,r,t)=0,\ \forall r\in\,]0,\mathscr{R}[,\ \forall t\geq 0$ (BC).

Eqs. (3.18) and (B.15) can be reconstructed using Eq. (B.22). If $\operatorname{rank}\left(\mathscr{L}_{f}\right)=R_f+p_{m,f}+p_{d,f}+1$, the extents are given by the linear transformation in Eq. (B.23).

B.1.6 Packed reactive separation columns

The volumetric heat $h_l^\varepsilon(z,t)$ is described by the PDE

$$\frac{\partial}{\partial t}h_l^\varepsilon + \frac{\partial}{\partial z}\left(v_{l,z}h_l^\varepsilon\right) = \left(-\boldsymbol{\Delta}\mathbf{H}_{r,l}^{\mathrm{T}}\right)\mathbf{r}_l^\varepsilon + \left(-\boldsymbol{\Delta}\mathbf{H}_{m,l}^{\mathrm{T}}\right)\boldsymbol{\phi}_{m,l}^{\varepsilon} + \phi_{ex,l}^{\varepsilon}. \tag{B.25}$$

Eq. (B.25) is subject to the following initial and advective boundary conditions:

$$h_l^\varepsilon(z,0) = h_{l,0}^\varepsilon(z), \quad \forall z > 0 \quad \text{(IC)},$$
$$h_l^\varepsilon(0,t) = h_{l,in}^\varepsilon(t), \quad \forall t \geq 0 \quad \text{(BC)}.$$

Furthermore, the system is subject to constraints related to the p_l intermediate inlets/outlets at the positions z_h[1]

$$h_l^\varepsilon(z_h,t) = \check{\mathbf{h}}_{in,h}^{\mathrm{T}}\frac{\mathbf{f}_{in,h}}{q_l(z_h,t)} + h_l^\varepsilon(z_h^-,t)\,\alpha_l(z_h,t) \qquad \forall h = 1,\ldots,p_l,\ \forall t \geq 0, \tag{B.26}$$

where $\check{\mathbf{h}}_{in,h}(t)$ is a $p_{l,h}$-dimensional vector, whose jth element is the molar heat of the jth liquid inlet at the hth intermediate inlet/outlet $\check{\mathbf{h}}_{in,h,j}(t) := \bar{\mathbf{c}}_{p,l,h,j}^{\mathrm{T}}(t)\,\mathbf{Z}_{in,h,j}(t)\left(T_{h,j}(t) - T_{ref}\right)$ at temperature $T_{h,j}(t)$, with the S-dimensional vector of average molar heat capacities $\bar{\mathbf{c}}_{p,l,h,j}(t) := \int_{T_{ref}}^{T_{h,j}(t)} \mathbf{c}_{p,l}(\theta)\,\mathrm{d}\theta \,/\left(T_{h,j}(t) - T_{ref}\right)$ between $T_{h,j}(t)$ and T_{ref}.

Let us define $\mathbf{z}_l^\varepsilon := \begin{bmatrix} \mathbf{c}_l^\varepsilon \\ h_l^\varepsilon \end{bmatrix}$. The effect of advection and intermediate outlet flows on the initial and advective boundary conditions can be computed by solving Eq. (B.17), with the initial and boundary conditions given by Eqs. (B.18) and (B.19), replacing the subscript f by l. In addition, for the intermediate inlets/outlets at the positions z_h,

$$\mathbf{z}_{ibc,l}^\varepsilon(z_h,t) = \begin{bmatrix} \mathbf{Z}_{in,h} \\ \check{\mathbf{h}}_{in,h}^{\mathrm{T}} \end{bmatrix}\frac{\mathbf{f}_{in,h}}{q_l(z_h,t)} + \mathbf{z}_{ibc,l}^\varepsilon(z_h^-,t)\,\alpha_l(z_h,t), \qquad \forall h = 1,\ldots,p_l,\ \forall t \geq 0.$$

Extent of heat exchange The extent of heat exchange $x_{ex,l}(z,t)$ represents the amount of energy that has transferred to phase L via heat exchange and is at position z at time t. This extent is described by Eq. (B.21), with the corresponding initial and boundary conditions, replacing the subscript f by l, and the constraints

$$x_{ex,l}(z_h,t) = x_{ex,l}(z_h^-,t)\,\alpha_l(z_h,t),\ \forall h = 1,\ldots,p_l,\ \forall t \geq 0.$$

[1] Eq. (B.26) results from the rearrangement of the heat balance $h_l^\varepsilon(z_h^-,t)q_l(z_h^-,t) + \check{\mathbf{h}}_{in,h}^{\mathrm{T}}\mathbf{f}_{in,h} = h_l^\varepsilon(z_h,t)q_l(z_h,t) + h_l^\varepsilon(z_h^-,t)\frac{q_{out,h}}{\varepsilon_l(z_h^-,t)}$ for $h_l^\varepsilon(z_h,t)$.

Eqs. (3.29) and (B.25) can be reconstructed using

$$\mathbf{z}_l^{\varepsilon} = \mathscr{L}_l \begin{bmatrix} \mathbf{x}_{r,l} \\ \mathbf{x}_{m,l} \\ x_{ex,l} \end{bmatrix} + \mathbf{z}_{ibc,l}^{\varepsilon}, \tag{B.27}$$

with $\mathscr{L}_l = \begin{bmatrix} \mathbf{N}_l^{\mathrm{T}} & \mathbf{E}_{m,l} & \mathbf{0}_{S_l} \\ -\boldsymbol{\Delta}\mathbf{H}_{r,l}^{\mathrm{T}} & -\boldsymbol{\Delta}\mathbf{H}_{m,l}^{\mathrm{T}} & 1 \end{bmatrix}$. If $\mathrm{rank}(\mathscr{L}_l) = R_l + p_{m,l} + 1$, the extents are given by the linear transformation

$$\begin{bmatrix} \mathbf{x}_{r,l} \\ \mathbf{x}_{m,l} \\ x_{ex,l} \end{bmatrix} = \mathscr{T}_l \, \delta\mathbf{z}_l^{\varepsilon}, \tag{B.28}$$

with $\mathscr{T}_l := \left(\mathscr{L}_l^{\mathrm{T}} \mathbf{W} \mathscr{L}_l\right)^{-1} \mathscr{L}_l^{\mathrm{T}} \mathbf{W}$, and $\delta\mathbf{z}_l^{\varepsilon} := \mathbf{z}_l^{\varepsilon} - \mathbf{z}_{ibc,l}^{\varepsilon}$.

B.1.7 Tray reactive separation columns

The volumetric heat $h_{l,n}^{\varepsilon}(t)$ on the nth tray is described by the ODE

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} h_{l,n}^{\varepsilon} + \Delta^{\omega} h_{l,n}^{\varepsilon} + \omega_{out,n} h_{l,n}^{\varepsilon} &= \left(-\boldsymbol{\Delta}\mathbf{H}_{r,l}^{\mathrm{T}}\right) \mathbf{r}_{l,n}^{\varepsilon} \\ &+ \left(-\boldsymbol{\Delta}\mathbf{H}_{m,l}^{\mathrm{T}}\right) \boldsymbol{\phi}_{m,l,n}^{\varepsilon} + \phi_{ex,l,n}^{\varepsilon} + \check{\mathbf{h}}_{in,n}^{\mathrm{T}} \frac{\mathbf{f}_{in,n}}{V_{t,n}}, \\ h_{l,n}^{\varepsilon}(0) &= h_{l,n,0}^{\varepsilon}. \end{aligned} \tag{B.29}$$

Multiplying Eq. (B.29) by $V_{t,n}$ leads to the following expression for $Q_{l,n} := V_{t,n} h_{l,n}^{\varepsilon}(t)$, the heat on nth tray

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} Q_{l,n} + \Delta^{\omega} Q_{l,n} + \omega_{out,n} Q_{l,n} &= \left(-\boldsymbol{\Delta}\mathbf{H}_{r,l}^{\mathrm{T}}\right) \mathbf{r}_{l,n}^{v} \\ &+ \left(-\boldsymbol{\Delta}\mathbf{H}_{m,l}^{\mathrm{T}}\right) \boldsymbol{\phi}_{m,l,n}^{v} + \phi_{ex,l,n}^{v} + \check{\mathbf{h}}_{in,n}^{\mathrm{T}} \mathbf{f}_{in,n}, \\ Q_{l,n}(0) &= Q_{l,n,0}, \end{aligned} \tag{B.30}$$

with $\phi_{ex,l,n}^{v}(t) := V_{t,n} \, \phi_{ex,l,n}^{\varepsilon}(t)$.

Let us define $\mathbf{z}_{l,n} := \begin{bmatrix} \mathbf{n}_{l,n} \\ Q_{l,n} \end{bmatrix}$. The effect of the outlet flows and transfer of material and energy between trays on the initial and inlet flow conditions can be computed as $\mathbf{z}_{iic,l,n}(t) := \begin{bmatrix} \mathbf{n}_{iic,l,n}(t) \\ Q_{iic,l,n}(t) \end{bmatrix}$ by solving the ODE

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} \mathbf{z}_{iic,l,n} + \Delta^{\omega} \mathbf{z}_{iic,l,n} + \omega_{out,n} \, \mathbf{z}_{iic,l,n} &= \begin{bmatrix} \mathbf{z}_{in,n} \\ \check{\mathbf{h}}_{in,n}^{\mathrm{T}} \end{bmatrix} \mathbf{f}_{in,n}, \\ \mathbf{z}_{iic,l,n}(0) &= \begin{bmatrix} \mathbf{n}_{l,n,0} \\ Q_{l,n,0} \end{bmatrix}. \end{aligned} \tag{B.31}$$

Extent of heat exchange The extent of heat exchange $x_{ex,l,n}(t)$ represents the amount of energy that has transferred to phase L via heat exchange and is on the nth tray at time t.

This extent is described by the ODE

$$\frac{\mathrm{d}}{\mathrm{d}t}x_{ex,l,n} + \Delta^{\omega}x_{ex,l,n} + \omega_{out,n}\,x_{ex,l,n} = \phi^{v}_{ex,l,n},$$
$$x_{ex,l,n}(0) = 0. \tag{B.32}$$

Eqs. (3.34) and (B.30) can be reconstructed using

$$\mathbf{z}_{l,n} = \mathscr{L}_l \begin{bmatrix} \mathbf{x}_{r,l,n} \\ \mathbf{x}_{m,l,n} \\ x_{ex,l,n} \end{bmatrix} + \mathbf{z}_{iic,l,n}, \tag{B.33}$$

with $\mathscr{L}_l = \begin{bmatrix} \mathbf{N}_l^{\mathrm{T}} & \mathbf{E}_{m,l} & \mathbf{0}_{S_l} \\ -\boldsymbol{\Delta}\mathbf{H}_{r,l}^{\mathrm{T}} & -\boldsymbol{\Delta}\mathbf{H}_{m,l}^{\mathrm{T}} & 1 \end{bmatrix}$. If $\mathrm{rank}(\mathscr{L}_l) = R_l + p_{m,l} + 1$, the extents are given by the linear transformation

$$\begin{bmatrix} \mathbf{x}_{r,l,n} \\ \mathbf{x}_{m,l,n} \\ x_{ex,l,n} \end{bmatrix} = \mathscr{T}_l\,\delta\mathbf{z}_{l,n}, \tag{B.34}$$

with $\mathscr{T}_l := \left(\mathscr{L}_l^{\mathrm{T}}\mathbf{W}\mathscr{L}_l\right)^{-1}\mathscr{L}_l^{\mathrm{T}}\mathbf{W}$, and $\delta\mathbf{z}_{l,n} := \mathbf{z}_{l,n} - \mathbf{z}_{iic,l,n}$.

B.1.8 Generic distributed reaction systems

The volumetric heat $h_f^{\varepsilon}(\boldsymbol{\chi}, t)$ is described by the PDE

$$\frac{\partial}{\partial t}h_f^{\varepsilon} + \nabla\cdot\left(\mathbf{v}_f h_f^{\varepsilon\,\mathrm{T}}\right) = \left(-\boldsymbol{\Delta}\mathbf{H}_{r,f}^{\mathrm{T}}\right)\mathbf{r}_f^{\varepsilon} + \left(-\boldsymbol{\Delta}\mathbf{H}_{m,f}^{\mathrm{T}}\right)\boldsymbol{\phi}_{m,f}^{\varepsilon}$$
$$+ \left(-\boldsymbol{\Delta}\mathbf{H}_{d,f}^{\mathrm{T}}\right)\boldsymbol{\phi}_{d,f}^{\varepsilon} + \phi_{c,f}^{\varepsilon} + \phi_{ex,f}^{\varepsilon}. \tag{B.35}$$

The existence of heat conduction in all three coordinates $\boldsymbol{\chi}$ requires defining a row vector of heat conduction fluxes of dimension 3, denoted $\mathbf{J}_{c,f}^{\varepsilon}(\boldsymbol{\chi}, t)$, which is described by the PDE

$$\nabla\cdot\mathbf{J}_{c,f}^{\varepsilon\,\mathrm{T}} = -\phi_{c,f}^{\varepsilon}, \tag{B.36}$$

with the conductive boundary conditions

$$\mathbf{J}_{c,f}^{\varepsilon}(\boldsymbol{\chi}, t)\,\vec{\mathbf{n}}(\boldsymbol{\chi}) = 0,\ \forall\boldsymbol{\chi} \in dBC,\ \forall t \geq 0.$$

Eq. (B.35) is subject to the following initial and advective boundary conditions:

$$h_f^{\varepsilon}(\boldsymbol{\chi}, 0) = h_{f,0}^{\varepsilon}(\boldsymbol{\chi}), \quad \forall\boldsymbol{\chi} \in IC \qquad \text{(IC)},$$
$$h_f^{\varepsilon}(\boldsymbol{\chi}, t) = h_{f,in}^{\varepsilon}(\boldsymbol{\chi}, t) + h_{d,f}^{\varepsilon}(\boldsymbol{\chi}, t) + h_{c,f}^{\varepsilon}(\boldsymbol{\chi}, t),$$
$$\forall\boldsymbol{\chi} \in aBC,\ \forall t \geq 0 \qquad \text{(BC)},$$

with $h^{\varepsilon}_{d,f}(\boldsymbol{\chi},t) := -\frac{\left(-\Delta\mathbf{H}^{\mathrm{T}}_{d,f}\right)\mathbf{J}^{\varepsilon}_{d,f}(\boldsymbol{\chi},t)\vec{\mathbf{n}}(\boldsymbol{\chi})}{\beta\mathbf{v}_f(\boldsymbol{\chi},t)^{\mathrm{T}}\vec{\mathbf{n}}(\boldsymbol{\chi})}$ and $h^{\varepsilon}_{c,f}(\boldsymbol{\chi},t) := -\frac{\mathbf{J}^{\varepsilon}_{c,f}(\boldsymbol{\chi},t)\vec{\mathbf{n}}(\boldsymbol{\chi})}{\beta\mathbf{v}_f(\boldsymbol{\chi},t)^{\mathrm{T}}\vec{\mathbf{n}}(\boldsymbol{\chi})}$. These initial and boundary conditions are also affected by those of Eqs. (3.41) and (B.36).

Let us define $\mathbf{z}^{\varepsilon}_f := \begin{bmatrix} \mathbf{c}^{\varepsilon}_f \\ h^{\varepsilon}_f \end{bmatrix}$. The effect of advection on the initial and advective boundary conditions can be computed as $\mathbf{z}^{\varepsilon}_{ibc,f}(\boldsymbol{\chi},t) := \begin{bmatrix} \mathbf{c}^{\varepsilon}_{ibc,f}(\boldsymbol{\chi},t) \\ h^{\varepsilon}_{ibc,f}(\boldsymbol{\chi},t) \end{bmatrix}$ by solving the PDE

$$\frac{\partial}{\partial t}\mathbf{z}^{\varepsilon}_{ibc,f} + \nabla\cdot\left(\mathbf{v}_f\,\mathbf{z}^{\varepsilon\,\mathrm{T}}_{ibc,f}\right) = \mathbf{0}_{S_f+1}, \tag{B.37}$$

with the initial and boundary conditions

$$\begin{aligned}
&\mathbf{z}^{\varepsilon}_{ibc,f}(\boldsymbol{\chi},0) = \begin{bmatrix} \mathbf{c}^{\varepsilon}_{f,0}(\boldsymbol{\chi}) \\ h^{\varepsilon}_{f,0}(\boldsymbol{\chi}) \end{bmatrix}, && \forall\boldsymbol{\chi}\in IC, && \text{(IC)},\\
&\mathbf{z}^{\varepsilon}_{ibc,f}(\boldsymbol{\chi},t) = \begin{bmatrix} \mathbf{c}^{\varepsilon}_{f,in}(\boldsymbol{\chi},t) \\ h^{\varepsilon}_{f,in}(\boldsymbol{\chi},t) \end{bmatrix}, && \forall\boldsymbol{\chi}\in aBC,\ \forall t\geq 0 && \text{(BC)}.
\end{aligned}$$

Extent of heat conduction The extent of heat conduction $x_{c,f}(\boldsymbol{\chi},t)$ represents the amount of energy that has transferred via heat conduction in phase F and is at position $\boldsymbol{\chi}$ at time t. This extent is described by the PDE

$$\frac{\partial}{\partial t}x_{c,f} + \nabla\cdot\left(\mathbf{v}_f\,x^{\mathrm{T}}_{c,f}\right) = \phi^{\varepsilon}_{c,f}, \tag{B.38}$$

with $x_{c,f}(\boldsymbol{\chi},0)=0$, $\forall\boldsymbol{\chi}\in IC$ (IC), and $x_{c,f}(\boldsymbol{\chi},t) = h^{\varepsilon}_{c,f}(\boldsymbol{\chi},t)$, $\forall\boldsymbol{\chi}\in aBC$, $\forall t\geq 0$ (BC).

Extent of heat exchange The extent of heat exchange $x_{ex,f}(\boldsymbol{\chi},t)$ represents the amount of energy that has transferred to phase F via heat exchange and is at position $\boldsymbol{\chi}$ at time t. This extent is described by the PDE

$$\frac{\partial}{\partial t}x_{ex,f} + \nabla\cdot\left(\mathbf{v}_f\,x^{\mathrm{T}}_{ex,f}\right) = \phi^{\varepsilon}_{ex,f}, \tag{B.39}$$

with $x_{ex,f}(\boldsymbol{\chi},0)=0$, $\forall\boldsymbol{\chi}\in IC$ (IC), and $x_{ex,f}(\boldsymbol{\chi},t)=0$, $\forall\boldsymbol{\chi}\in aBC$, $\forall t\geq 0$ (BC).

Eqs. (3.40) and (B.35) can be reconstructed using Eq. (B.22). If $\operatorname{rank}\left(\mathscr{L}_f\right) = R_f + p_{m,f} + p_{d,f} + 1$, the extents are given by the linear transformation in Eq. (B.23).

C Appendix of Chapter 4

C.1 Experimental Extents with Minimal Variance

It is known that any optimization problem with the decision variables $\mathbf{t}_{r,i}$ and constrained by the linear equality constraints $\mathbf{A}\mathbf{t}_{r,i} = \mathbf{b}$ can be converted to an equivalent optimization problem, in which these constraints are discarded and $\mathbf{t}_{r,i}$ is replaced by $\mathbf{t}_{r,i,s} + \mathbf{F}\mathbf{v}_{r,i}$, where $\mathbf{v}_{r,i}$ are the new decision variables, $\mathbf{t}_{r,i,s}$ is a particular solution to $\mathbf{A}\mathbf{t}_{r,i} = \mathbf{b}$ and the columns of $\mathbf{F}$ are a basis of the null space of $\mathbf{A}$ [80].

It is clear that $\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}^{-1}\mathbf{S}_i^{\mathrm{T}}\mathbf{N}_i^{\mathrm{T}}\left(\mathbf{N}_i\mathbf{S}_i\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}^{-1}\mathbf{S}_i^{\mathrm{T}}\mathbf{N}_i^{\mathrm{T}}\right)^{-1}\mathbf{e}_i$ is a particular solution to the linear equality constraints $\mathbf{N}_i\mathbf{S}_i\mathbf{t}_{r,i} = \mathbf{e}_i$ and there is a $W_i \times \left(W_i - R_i\right)$ matrix $\mathbf{P}_i$ whose columns are a basis of the null space of $\mathbf{N}_i\mathbf{S}_i$. Then, if these constraints are discarded and $\mathbf{t}_{r,i}$ is replaced by

$$\begin{aligned}\mathbf{t}_{r,i} &= \boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}^{-1}\mathbf{S}_i^{\mathrm{T}}\mathbf{N}_i^{\mathrm{T}}\left(\mathbf{N}_i\mathbf{S}_i\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}^{-1}\mathbf{S}_i^{\mathrm{T}}\mathbf{N}_i^{\mathrm{T}}\right)^{-1}\mathbf{e}_i + \mathbf{P}_i\mathbf{v}_{r,i} \\ &= \boldsymbol{\mathscr{T}}_{r,i}^{\mathrm{T}}\mathbf{e}_i + \mathbf{P}_i\mathbf{v}_{r,i},\end{aligned} \tag{C.1}$$

where $\mathbf{v}_{r,i}$ are the new decision variables, the constrained optimization Problem (4.39) can be converted to the equivalent unconstrained optimization problem

$$\begin{aligned}\min_{\mathbf{v}_{r,i}} \quad \sigma_{\tilde{x}_{r,i},u}^2(\mathbf{v}_{r,i}) &= \left(\mathbf{e}_i^{\mathrm{T}}\boldsymbol{\mathscr{T}}_{r,i} + \mathbf{v}_{r,i}^{\mathrm{T}}\mathbf{P}_i^{\mathrm{T}}\right)\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}\left(\boldsymbol{\mathscr{T}}_{r,i}^{\mathrm{T}}\mathbf{e}_i + \mathbf{P}_i\mathbf{v}_{r,i}\right) \\ &= \mathbf{v}_{r,i}^{\mathrm{T}}\mathbf{P}_i^{\mathrm{T}}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}\mathbf{P}_i\mathbf{v}_{r,i} + 2\mathbf{v}_{r,i}^{\mathrm{T}}\mathbf{P}_i^{\mathrm{T}}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}\boldsymbol{\mathscr{T}}_{r,i}^{\mathrm{T}}\mathbf{e}_i + \mathbf{e}_i^{\mathrm{T}}\boldsymbol{\mathscr{T}}_{r,i}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}\boldsymbol{\mathscr{T}}_{r,i}^{\mathrm{T}}\mathbf{e}_i.\end{aligned} \tag{C.2}$$

Since Problem (C.2) is unconstrained and the Hessian matrix of $\sigma_{\tilde{x}_{r,i},u}^2(\mathbf{v}_{r,i})$, $2\mathbf{P}_i^{\mathrm{T}}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}\mathbf{P}_i$, is positive definite for all $\mathbf{v}_{r,i}$, the solution $\mathbf{v}_{r,i}^*$ to this problem is given by the stationarity condition

$$\mathbf{0}_{W_i - R_i} = 2\mathbf{P}_i^{\mathrm{T}}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}\mathbf{P}_i\mathbf{v}_{r,i} + 2\mathbf{P}_i^{\mathrm{T}}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}\boldsymbol{\mathscr{T}}_{r,i}^{\mathrm{T}}\mathbf{e}_i. \tag{C.3}$$

Since the matrix $\mathbf{P}_i^{\mathrm{T}}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}\mathbf{P}_i$ is invertible and $\mathbf{N}_i\mathbf{S}_i\mathbf{P}_i = \mathbf{0}_{R_i\times(W_i-R_i)}$,

$$\begin{aligned}\mathbf{v}_{r,i}^{*} &= -\left(\mathbf{P}_i^{\mathrm{T}}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}\mathbf{P}_i\right)^{-1}\mathbf{P}_i^{\mathrm{T}}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}\boldsymbol{\mathscr{T}}_{r,i}^{\mathrm{T}}\mathbf{e}_i \\ &= -\left(\mathbf{P}_i^{\mathrm{T}}\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}\mathbf{P}_i\right)^{-1}\mathbf{P}_i^{\mathrm{T}}\mathbf{S}_i^{\mathrm{T}}\mathbf{N}_i^{\mathrm{T}}\left(\mathbf{N}_i\mathbf{S}_i\boldsymbol{\Sigma}_{\tilde{\mathbf{y}}_i}^{-1}\mathbf{S}_i^{\mathrm{T}}\mathbf{N}_i^{\mathrm{T}}\right)^{-1}\mathbf{e}_i \\ &= \mathbf{0}_{W_i-R_i},\end{aligned} \tag{C.4}$$

and the solution $\mathbf{t}_{r,i}^{*}$ of the constrained optimization Problem (4.39) is

$$\begin{aligned}\mathbf{t}_{r,i}^{*} &= \boldsymbol{\mathscr{T}}_{r,i}^{\mathrm{T}}\mathbf{e}_i + \mathbf{P}_i\mathbf{v}_{r,i}^{*} \\ &= \boldsymbol{\mathscr{T}}_{r,i}^{\mathrm{T}}\mathbf{e}_i.\end{aligned} \tag{C.5}$$

C.2 Proof of Unbiased Rate Estimation

This proof is constructed via induction.

For $\hat{r}^0(\tilde{z})$, it holds that

$$\hat{r}^0(\tilde{z}) = 0 = -\left(\sum_{k=0}^{-1}\mathrm{B}_{\hat{r}^k}(\tilde{z})\right), \tag{C.6}$$

$$\mathrm{B}_{\hat{r}^0}(\tilde{z}) = \mathrm{E}\left[\hat{r}^0(\tilde{Z})|\tilde{Z}\sim\mathscr{N}(\tilde{z},\sigma^2)\right] - r(\tilde{z}) = -r(\tilde{z}). \tag{C.7}$$

Hence, for $\hat{r}^{n+1}(\tilde{z})$, with $n = 0, 1, \ldots$, it holds that

$$\hat{r}^{n+1}(\tilde{z}) = \hat{r}^n(\tilde{z}) - \mathrm{B}_{\hat{r}^n}(\tilde{z}) = -\left(\sum_{k=0}^{n-1}\mathrm{B}_{\hat{r}^k}(\tilde{z})\right) - \mathrm{B}_{\hat{r}^n}(\tilde{z}) = -\left(\sum_{k=0}^{n}\mathrm{B}_{\hat{r}^k}(\tilde{z})\right), \tag{C.8}$$

$$\begin{aligned}\mathrm{B}_{\hat{r}^{n+1}}(\tilde{z}) &= \mathrm{E}\left[\hat{r}^{n+1}(\tilde{Z})|\tilde{Z}\sim\mathscr{N}(\tilde{z},\sigma^2)\right] - r(\tilde{z}) \\ &= \mathrm{E}\left[\hat{r}^{n}(\tilde{Z})|\tilde{Z}\sim\mathscr{N}(\tilde{z},\sigma^2)\right] - r(\tilde{z}) - \mathrm{E}\left[\mathrm{B}_{\hat{r}^n}(\tilde{Z})|\tilde{Z}\sim\mathscr{N}(\tilde{z},\sigma^2)\right] \\ &= \mathrm{B}_{\hat{r}^n}(\tilde{z}) - \mathrm{E}\left[\mathrm{B}_{\hat{r}^n}(\tilde{Z})|\tilde{Z}\sim\mathscr{N}(\tilde{z},\sigma^2)\right].\end{aligned} \tag{C.9}$$

Let us express $\mathrm{B}_{\hat{r}^n}(\tilde{z})$ as the sum

$$\mathrm{B}_{\hat{r}^n}(\tilde{z}) = \sum_{j=1}^{n+1}\phi_{n+1,j}\mathscr{E}_j(\tilde{z}). \tag{C.10}$$

In the case of $\mathrm{B}_{\hat{r}^0}(\tilde{z})$, one can verify that

$$\mathrm{B}_{\hat{r}^0}(\tilde{z}) = -r(\tilde{z}) = -\mathscr{E}_1(\tilde{z}), \tag{C.11}$$

which means that

$$\phi_{1,1} = -1. \tag{C.12}$$

In the case of $\mathrm{B}_{\hat{r}^n}(\tilde{z})$, with $n = 1, 2, \ldots$, one can also verify that

$$\begin{aligned}
\mathrm{B}_{\hat{r}^n}(\tilde{z}) &= \mathrm{B}_{\hat{r}^{n-1}}(\tilde{z}) - \mathrm{E}\left[\mathrm{B}_{\hat{r}^{n-1}}(\tilde{Z}) | \tilde{Z} \sim \mathcal{N}(\tilde{z}, \sigma^2)\right] \\
&= \sum_{j=1}^{n} \phi_{n,j} \mathscr{E}_j(\tilde{z}) - \left(\sum_{j=1}^{n} \phi_{n,j} \, \mathrm{E}\left[\mathscr{E}_j(\tilde{Z}) | \tilde{Z} \sim \mathcal{N}(\tilde{z}, \sigma^2)\right] \right) \\
&= \sum_{j=1}^{n} \phi_{n,j} \mathscr{E}_j(\tilde{z}) - \left(\sum_{j=1}^{n} \phi_{n,j} \mathscr{E}_{j+1}(\tilde{z}) \right) \\
&= \sum_{j=1}^{n} \phi_{n,j} \mathscr{E}_j(\tilde{z}) - \left(\sum_{j=2}^{n+1} \phi_{n,j-1} \mathscr{E}_j(\tilde{z}) \right) \\
&= \sum_{j=1}^{n+1} \phi_{n+1,j} \mathscr{E}_j(\tilde{z}),
\end{aligned} \tag{C.13}$$

which means that

$$\phi_{n+1,j} = \begin{cases} \phi_{n,1}, & j = 1 \\ \phi_{n,j} - \phi_{n,j-1}, & j = 2, \ldots, n \\ -\phi_{n,n}, & j = n+1 \end{cases}. \tag{C.14}$$

Moreover, one can show that

$$\sum_{k=0}^{n} \mathrm{B}_{\hat{r}^k}(\tilde{z}) = \sum_{k=0}^{n} \left(\sum_{j=1}^{k+1} \phi_{k+1,j} \mathscr{E}_j(\tilde{z}) \right) = \sum_{j=1}^{n+1} \left(\sum_{k=j-1}^{n} \phi_{k+1,j} \right) \mathscr{E}_j(\tilde{z}) = \sum_{j=1}^{n+1} \Phi_{n+1,j} \mathscr{E}_j(\tilde{z}), \tag{C.15}$$

by defining

$$\Phi_{n+1,j} = \sum_{k=j}^{n+1} \phi_{k,j}. \tag{C.16}$$

In particular, for $n = 0$ and $n = 1$,

$$\Phi_{1,1} = \phi_{1,1} = -1 = (-1)^1 \binom{1}{1}, \tag{C.17}$$

$$\Phi_{2,1} = \phi_{1,1} + \phi_{2,1} = \phi_{1,1} + \phi_{1,1} = -2 = (-1)^1 \binom{2}{1}, \tag{C.18}$$

$$\Phi_{2,2} = \phi_{2,2} = -\phi_{1,1} = 1 = (-1)^2 \binom{2}{2}. \tag{C.19}$$

In general, for $n = 2, 3, \ldots$, one can show that

$$\begin{aligned}
\Phi_{n+1,j} &= \sum_{k=j}^{n} \phi_{k,j} + \phi_{n+1,j} \\
&= \begin{cases} \Phi_{n,j} + \phi_{n+1,j}, & j = 1, \ldots, n \\ \phi_{n+1,j}, & j = n+1 \end{cases} \\
&= \begin{cases} \Phi_{n,j} + \phi_{n,1}, & j = 1 \\ \Phi_{n,j} + \phi_{n,j} - \phi_{n,j-1}, & j = 2, \ldots, n \\ -\phi_{n,n}, & j = n+1 \end{cases} \\
&= \begin{cases} \Phi_{n,1} + \Phi_{n,1} - \Phi_{n-1,1}, & j = 1 \\ \Phi_{n,j} + \Phi_{n,j} - \Phi_{n-1,j} - \Phi_{n,j-1} + \Phi_{n-1,j-1}, & j = 2, \ldots, n-1 \\ \Phi_{n,n} + \Phi_{n,n} - \Phi_{n,n-1} + \Phi_{n-1,n-1}, & j = n \\ -\Phi_{n,n}, & j = n+1 \end{cases} \\
&= \begin{cases} 2\Phi_{n,1} - \Phi_{n-1,1}, & j = 1 \\ 2\Phi_{n,j} - \Phi_{n-1,j} - \Phi_{n,j-1} + \Phi_{n-1,j-1}, & j = 2, \ldots, n-1 \\ 2\Phi_{n,n} - \Phi_{n,n-1} + \Phi_{n-1,n-1}, & j = n \\ -\Phi_{n,n}, & j = n+1 \end{cases},
\end{aligned} \tag{C.20}$$

therefore, if

$$\begin{cases} \Phi_{n-1,j} = (-1)^j \binom{n-1}{j}, & j = 1, \ldots, n-1 \\ \Phi_{n,j} = (-1)^j \binom{n}{j}, & j = 1, \ldots, n \end{cases}, \tag{C.21}$$

which is satisfied for $n=2$, then it follows that

$$\begin{aligned}
\Phi_{n+1,j} &= \begin{cases} 2(-1)^1\binom{n}{1}-(-1)^1\binom{n-1}{1}, & j=1 \\ 2(-1)^j\binom{n}{j}-(-1)^j\binom{n-1}{j}-(-1)^{j-1}\left(\binom{n}{j-1}-\binom{n-1}{j-1}\right), & j=2,\dots,n-1 \\ 2(-1)^n\binom{n}{n}-(-1)^{n-1}\left(\binom{n}{n-1}-\binom{n-1}{n-1}\right), & j=n \\ -(-1)^n\binom{n}{n}, & j=n+1 \end{cases} \\
&= \begin{cases} -2n+(n-1), & j=1 \\ (-1)^j\left(2\binom{n}{j}-\binom{n-1}{j}+\binom{n}{j-1}-\binom{n-1}{j-1}\right), & j=2,\dots,n-1 \\ (-1)^n(2+n-1), & j=n \\ (-1)^{n+1}, & j=n+1 \end{cases} \\
&= \begin{cases} -(n+1), & j=1 \\ (-1)^j\left(\binom{n}{j}+\binom{n}{j-1}\right), & j=2,\dots,n-1 \\ (-1)^n(n+1), & j=n \\ (-1)^{n+1}, & j=n+1 \end{cases} \\
&= (-1)^j\binom{n+1}{j}, \qquad j=1,\dots,n+1,
\end{aligned} \tag{C.22}$$

which implies that this condition is satisfied for all $n=0,1,\dots$. Consequently,

$$\hat{r}^{n+1}(\tilde{z}) = -\left(\sum_{k=0}^{n}\mathrm{B}_{\hat{r}^k}(\tilde{z})\right) = -\left(\sum_{j=1}^{n+1}\Phi_{n+1,j}\mathscr{E}_j(\tilde{z})\right) = \sum_{j=1}^{n+1}(-1)^{j+1}\binom{n+1}{j}\mathscr{E}_j(\tilde{z}). \tag{C.23}$$

C.3 Unbiased Rate Estimation via the Delta Method

First, let us show how the delta method can be applied to the unbiased estimation of the rate r. The delta method requires that an n^{th}-degree Taylor series expansion of the rate r around z be valid for any value of $\tilde{z}$ with a probability density greater than α, that is,

$$r(\tilde{z}) = \sum_{k=0}^{n}\frac{r^{(k)}(z)}{k!}(\tilde{z}-z)^k, \qquad \forall\tilde{z}:\frac{1}{\sigma}\phi\left(\frac{\tilde{z}-z}{\sigma}\right)>\alpha, \tag{C.24}$$

where ϕ is the probability density function of the standard normal distribution. In that case,

$$\begin{aligned}
\mathrm{E}\left[r(Z)|Z\sim\mathcal{N}(z,\sigma^2)\right] &= \int_{-\infty}^{\infty} r(\tilde{z})\frac{1}{\sigma}\phi\left(\frac{\tilde{z}-z}{\sigma}\right)\mathrm{d}\tilde{z} \\
&= \sum_{k=0}^{n}\frac{r^{(k)}(z)}{k!}\sigma^k\int_{-\infty}^{\infty}\left(\frac{\tilde{z}-z}{\sigma}\right)^k\frac{1}{\sigma}\phi\left(\frac{\tilde{z}-z}{\sigma}\right)\mathrm{d}\tilde{z} \\
&= \sum_{k=0}^{n}\frac{r^{(k)}(z)}{k!}\sigma^k\int_{-\infty}^{\infty}x^k\phi\left(x\right)\mathrm{d}x \\
&= \sum_{k=0}^{\lfloor n/2\rfloor}\frac{r^{(2k)}(z)}{(2k)!}\sigma^{2k}\left(2k-1\right)!! \\
&= r(z)+\sum_{k=1}^{\lfloor n/2\rfloor}\frac{r^{(2k)}(z)}{(2k)!}\sigma^{2k}\left(2k-1\right)!!,
\end{aligned} \tag{C.25}$$

where $k!!$ denotes the double factorial of k, which is the product of all the odd integers up to k if k is odd. This implies that

$$\mathrm{E}\left[r(Z)-\sum_{k=1}^{\lfloor n/2\rfloor}\frac{r^{(2k)}(z)}{(2k)!}\sigma^{2k}\left(2k-1\right)!!|Z\sim\mathcal{N}(z,\sigma^2)\right]=r(z), \tag{C.26}$$

meaning that $r(Z)-\sum_{k=1}^{\lfloor n/2\rfloor}\frac{r^{(2k)}(z)}{(2k)!}\sigma^{2k}\left(2k-1\right)!!$ is an unbiased estimator of $r(z)$. However, since z is unknown, the estimator $\hat{r}^{\delta}$ given by the delta method will have to correspond to the substitution of z by $\tilde{z}$ in the expression of this estimator, which yields the estimate

$$\hat{r}^{\delta}(\tilde{z})=r(\tilde{z})-\sum_{k=1}^{\lfloor n/2\rfloor}\frac{r^{(2k)}(\tilde{z})}{(2k)!}\sigma^{2k}\left(2k-1\right)!!=2r(\tilde{z})-\sum_{k=0}^{\lfloor n/2\rfloor}\frac{r^{(2k)}(\tilde{z})}{(2k)!}\sigma^{2k}\left(2k-1\right)!!. \tag{C.27}$$

Then, taking Eq. (C.25) into account yields the following result:

$$\begin{aligned}
\hat{r}^{\delta}(\tilde{z}) &= 2r(\tilde{z})-\mathrm{E}\left[r(\tilde{Z})|\tilde{Z}\sim\mathcal{N}(\tilde{z},\sigma^2)\right] \\
&= 2\mathscr{E}_1(\tilde{z})-\mathscr{E}_2(\tilde{z}) \\
&= \hat{r}^2(\tilde{z}).
\end{aligned} \tag{C.28}$$

Hence, the application of the delta method to unbiased rate estimation is equivalent to a particular case of the aforementioned more general method.

C.4 Unbiased Rate Estimation via the Extent-based Incremental Approach

Let us show that, if Eq. (4.57) is satisfied and all the measurements $\tilde{\mathbf{z}}(t)$ needed to compute $\hat{r}_\ell\big(\tilde{\mathbf{z}}(t),\boldsymbol{\theta}\big)$ are uncorrelated and corrupted by zero-mean noise, then $\hat{r}_\ell\big(\tilde{\mathbf{z}}(t),\boldsymbol{\theta}\big)$ is an unbiased estimate of $r_\ell\big(\mathbf{z}(t),\boldsymbol{\theta}\big)$, and Eq. (4.58) holds.

According to Section 4.3.2, $\hat{r}_{\ell,j,s}\big(\tilde{z}_s(t),\boldsymbol{\theta}\big)$ can be assumed to be an unbiased estimate of $r_{\ell,j,s}\big(z_s(t),\boldsymbol{\theta}\big)$ for all $s=1,\dots,S+1$ if $\tilde{z}_s(t)$ is corrupted by zero-mean noise. Hence, if Eq. (4.57) is satisfied and all the measurements $\tilde{\mathbf{z}}(t)$ needed to compute $\hat{r}_\ell\big(\tilde{\mathbf{z}}(t),\boldsymbol{\theta}\big)$ are uncorrelated and corrupted by zero-mean noise, then

$$\begin{aligned}
\mathrm{E}\left[\hat{r}_\ell\big(\tilde{\mathbf{z}}(t),\boldsymbol{\theta}\big)\right] &= \mathrm{E}\left[\sum_{j=1}^{J} w_{\ell,j}\prod_{s=1}^{S+1}\hat{r}_{\ell,j,s}\big(\tilde{z}_s(t),\boldsymbol{\theta}\big)\right]\\
&= \sum_{j=1}^{J} w_{\ell,j}\prod_{s=1}^{S+1}\mathrm{E}\left[\hat{r}_{\ell,j,s}\big(\tilde{z}_s(t),\boldsymbol{\theta}\big)\right]\\
&= \sum_{j=1}^{J} w_{\ell,j}\prod_{s=1}^{S+1} r_{\ell,j,s}\big(z_s(t),\boldsymbol{\theta}\big)\\
&= r_\ell\big(\mathbf{z}(t),\boldsymbol{\theta}\big), \qquad \forall \ell = 0,\dots,L,
\end{aligned} \tag{C.29}$$

which shows that $\hat{r}_\ell\big(\tilde{\mathbf{z}}(t),\boldsymbol{\theta}\big)$ is indeed an unbiased estimate of $r_\ell\big(\mathbf{z}(t),\boldsymbol{\theta}\big)$.

Then,

$$\begin{aligned}
\lim_{h\to 0}\mathrm{E}\left[\hat{d}_\ell(t,\boldsymbol{\theta})\right] &= \lim_{h\to 0}\sum_{m=0}^{\frac{t}{h}} h\gamma_m r_\ell\big(\mathbf{z}(t_m),\boldsymbol{\theta}\big)\frac{x_{ic}(t)/V(t)}{x_{ic}(t_m)/V(t_m)}\\
&= \int_0^t r_\ell(\mathbf{z}(\tau),\boldsymbol{\theta})\frac{x_{ic}(t)/V(t)}{x_{ic}(\tau)/V(\tau)}\,\mathrm{d}\tau\\
&= d_\ell(t,\boldsymbol{\theta}), \qquad \forall \ell = 0,\dots,L,
\end{aligned} \tag{C.30}$$

and, if the measurements at different time instants are uncorrelated,

$$\begin{aligned}
\lim_{h\to 0}\mathrm{Var}\left[\hat{d}_\ell(t,\boldsymbol{\theta})\right] &= \lim_{h\to 0}\sum_{m=0}^{\frac{t}{h}} h^2\gamma_m^2\,\mathrm{Var}\left[\hat{r}_\ell\big(\tilde{\mathbf{z}}(t_m),\boldsymbol{\theta}\big)\right]\left(\frac{x_{ic}(t)/V(t)}{x_{ic}(t_m)/V(t_m)}\right)^2\\
&= \lim_{h\to 0} th\frac{\sum_{m=0}^{\frac{t}{h}}\gamma_m^2\,\mathrm{Var}\left[\hat{r}_\ell\big(\tilde{\mathbf{z}}(t_m),\boldsymbol{\theta}\big)\right]\left(\frac{x_{ic}(t)/V(t)}{x_{ic}(t_m)/V(t_m)}\right)^2}{\frac{t}{h}}\\
&= 0, \qquad \forall \ell = 0,\dots,L,
\end{aligned} \tag{C.31}$$

which implies that Eq. (4.58) holds.

C.5 Global Solution to the Identification Problem

The following equations show that, if r is the i^{th} reaction rate and $\boldsymbol{\alpha}^*$ and $\boldsymbol{\theta}^*$ are the true values of the parameters, a global minimum of $J(\boldsymbol{\alpha},\boldsymbol{\theta})$ is attained for these values of the parameters, when $h \to 0$:

$$\begin{aligned}
\lim_{h\to 0}\frac{J(\boldsymbol{\alpha},\boldsymbol{\theta})}{H} &= \lim_{H\to\infty}\sum_{m=1}^{H}\frac{1}{H}\left(d_0(t_m,\boldsymbol{\theta})+\sum_{\ell=1}^{L}\alpha_\ell d_\ell(t_m,\boldsymbol{\theta})-\frac{\tilde{x}_{r,i}(t_m)}{V(t_m)}\right)^2\\
&= \lim_{H\to\infty}\sum_{m=1}^{H}\frac{1}{H}\left(\frac{x_r(t_m,\boldsymbol{\alpha},\boldsymbol{\theta})-x_{r,i}(t_m)}{V(t_m)}+\frac{\mathrm{E}\left[\tilde{x}_{r,i}(t_m)\right]-\tilde{x}_{r,i}(t_m)}{V(t_m)}\right)^2\\
&= \sum_{m=1}^{H}\frac{1}{H}\left(\frac{x_r(t_m,\boldsymbol{\alpha},\boldsymbol{\theta})-x_{r,i}(t_m)}{V(t_m)}\right)^2\\
&\quad+\lim_{H\to\infty}\sum_{m=1}^{H}\frac{1}{H}\left(\frac{\mathrm{E}\left[\tilde{x}_{r,i}(t_m)\right]-\tilde{x}_{r,i}(t_m)}{V(t_m)}\right)^2\\
&\quad+\lim_{H\to\infty}\sum_{m=1}^{H}\frac{2}{H}\frac{x_r(t_m,\boldsymbol{\alpha},\boldsymbol{\theta})-x_{r,i}(t_m)}{V(t_m)}\frac{\mathrm{E}\left[\tilde{x}_{r,i}(t_m)\right]-\tilde{x}_{r,i}(t_m)}{V(t_m)}\\
&= \sum_{m=1}^{H}\frac{1}{H}\left(\frac{x_r(t_m,\boldsymbol{\alpha},\boldsymbol{\theta})-x_{r,i}(t_m)}{V(t_m)}\right)^2\\
&\quad+\sum_{m=1}^{H}\frac{1}{H}\mathrm{E}\left[\left(\frac{\tilde{x}_{r,i}(t_m)}{V(t_m)}-\mathrm{E}\left[\frac{\tilde{x}_{r,i}(t_m)}{V(t_m)}\right]\right)^2\right]\\
&\quad+\sum_{m=1}^{H}\frac{2}{H}\frac{x_r(t_m,\boldsymbol{\alpha},\boldsymbol{\theta})-x_{r,i}(t_m)}{V(t_m)}\frac{\mathrm{E}\left[\tilde{x}_{r,i}(t_m)\right]-\mathrm{E}\left[\tilde{x}_{r,i}(t_m)\right]}{V(t_m)}\\
&= \sum_{m=1}^{H}\frac{1}{H}\left(\frac{x_r(t_m,\boldsymbol{\alpha},\boldsymbol{\theta})-x_{r,i}(t_m)}{V(t_m)}\right)^2+\mathrm{Var}\left[\frac{\tilde{x}_{r,i}(t)}{V(t)}\right],\quad\forall\boldsymbol{\alpha},\boldsymbol{\theta},
\end{aligned}\tag{C.32}$$

$$\begin{aligned}
\lim_{h\to 0}\frac{J(\boldsymbol{\alpha}^*,\boldsymbol{\theta}^*)}{H} &= \sum_{m=1}^{H}\frac{1}{H}\left(\frac{x_r(t_m,\boldsymbol{\alpha}^*,\boldsymbol{\theta}^*)-x_{r,i}(t_m)}{V(t_m)}\right)^2+\mathrm{Var}\left[\frac{\tilde{x}_{r,i}(t)}{V(t)}\right]=\mathrm{Var}\left[\frac{\tilde{x}_{r,i}(t)}{V(t)}\right]\\
&\le \lim_{h\to 0}\frac{J(\boldsymbol{\alpha},\boldsymbol{\theta})}{H},\quad\forall\boldsymbol{\alpha},\boldsymbol{\theta}.
\end{aligned}\tag{C.33}$$

C.6 Proof of the Reformulation as a Convex Optimization Problem

Let us assume that the optimal $\Delta\boldsymbol{\theta}$ is in the compact set $\mathscr{C}=\left\{\mathbf{y}:\sum_{\mathbf{q}\in\mathscr{K}_2}c_{\mathbf{q}}\mathbf{y}^{\mathbf{q}}\ge 0\right\}$. This proof shows that, by using the equivalence of nonnegative polynomials and conical combination of sum-of-squares polynomials on a compact set [102], Problem (4.78) can be

written as the convex semidefinite program (SDP)

$$\max_{\zeta,\mathbf{Q}_0,\mathbf{Q}_1} \quad \zeta \tag{C.34a}$$

$$\text{s.t.} \quad \mathbf{Q}_0 \succeq \mathbf{0}_{s(N,d)\times s(N,d)} \tag{C.34b}$$

$$\mathbf{Q}_1 \succeq \mathbf{0}_{s(N,d-1)\times s(N,d-1)} \tag{C.34c}$$

$$b_{\mathbf{k}} - a_{\mathbf{k}}\zeta = \operatorname{tr}\left(\mathbf{R}_{0,\mathbf{k}}\mathbf{Q}_0\right) + \sum_{\substack{\mathbf{q}\in\mathscr{K}_2 \\ \mathbf{k}-\mathbf{q}\in\mathscr{K}_{2d}}} c_{\mathbf{q}} \operatorname{tr}\left(\mathbf{R}_{1,\mathbf{k}-\mathbf{q}}\mathbf{Q}_1\right), \quad \forall \mathbf{k}\in\mathscr{K}_{2d}, \tag{C.34d}$$

where $\mathbf{R}_{0,\mathbf{k}}$ and $\mathbf{R}_{1,\mathbf{k}}$ are localizing matrices such that

$$\sum_{\mathbf{k}\in\mathscr{K}_{2d}} \mathbf{R}_{0,\mathbf{k}}\,\Delta\boldsymbol{\theta}^{\mathbf{k}} = \mathbf{v}_d(\Delta\boldsymbol{\theta})\mathbf{v}_d(\Delta\boldsymbol{\theta})^{\mathrm{T}}, \tag{C.35a}$$

$$\sum_{\mathbf{k}\in\mathscr{K}_{2d}} \mathbf{R}_{1,\mathbf{k}}\,\Delta\boldsymbol{\theta}^{\mathbf{k}} = \mathbf{v}_{d-1}(\Delta\boldsymbol{\theta})\mathbf{v}_{d-1}(\Delta\boldsymbol{\theta})^{\mathrm{T}}, \tag{C.35b}$$

with the $s(N,d)$-dimensional vector of monomials up to degree d in the N variables $\Delta\boldsymbol{\theta}$ defined as

$$\mathbf{v}_d(\Delta\boldsymbol{\theta})^{\mathrm{T}} := \left(1, \Delta\theta_1, \cdots, \Delta\theta_N, \Delta\theta_1^2, \cdots, \Delta\theta_1\Delta\theta_N, \cdots, \Delta\theta_N^2, \cdots, \Delta\theta_1^d, \cdots, \Delta\theta_N^d\right). \tag{C.36}$$

Note that, if $P_a(\Delta\boldsymbol{\theta})$ and $P_b(\Delta\boldsymbol{\theta})$ are univariate polynomials ($N = 1$), Problems (4.78) and (C.34) are equivalent with $d = n(L+1)$. In the case of multivariate polynomials ($N \geq 2$), the equivalence between these optimization problems is obtained for some $d \geq n(L+1)$, by starting with $d = n(L+1)$ and increasing d until $\operatorname{rank}\left(\sum_{\mathbf{k}\in\mathscr{K}_{2d}} \mathbf{R}_{0,\mathbf{k}}\,\mu_{\mathbf{k}}\right) = \operatorname{rank}\left(\sum_{\mathbf{k}\in\mathscr{K}_{2d}} \mathbf{R}_{1,\mathbf{k}}\,\mu_{\mathbf{k}}\right)$, where $\mu_{\mathbf{k}}$ is the dual variable of the constraint in Eq. (C.34d), $\forall \mathbf{k} \in \mathscr{K}_{2d}$ [158].

Let us proceed with the proof. Since it is assumed that the optimal $\Delta\boldsymbol{\theta}$ is in a compact set $\mathscr{C} = \left\{\mathbf{y} : \sum_{\mathbf{q}\in\mathscr{K}_2} c_{\mathbf{q}}\mathbf{y}^{\mathbf{q}} \geq 0\right\}$, the feasibility of the constraint on the cost function $\bar{J}_c(\Delta\boldsymbol{\theta})$,

$$\bar{J}_c(\Delta\boldsymbol{\theta}) - \zeta \geq 0, \ \forall \Delta\boldsymbol{\theta} \in \mathscr{C}, \tag{C.37}$$

is still equivalent to the nonnegativity of a polynomial in $\Delta\boldsymbol{\theta}$, as follows:

$$\det\left(\mathbf{M}(\Delta\boldsymbol{\theta})\right) - \det\left(\mathbf{H}_c(\Delta\boldsymbol{\theta})\right)\zeta \geq 0, \ \forall \Delta\boldsymbol{\theta} \in \mathscr{C}. \tag{C.38}$$

Let us introduce $a_{\mathbf{k}}$ and $b_{\mathbf{k}}$ such that they correspond to the coefficients of the polyno-

mials $\det\left(\mathbf{H}_c(\Delta\boldsymbol{\theta})\right)$ and $\det\left(\mathbf{M}(\Delta\boldsymbol{\theta})\right)$, respectively, which means that they satisfy

$$\det\left(\mathbf{H}_c(\Delta\boldsymbol{\theta})\right) = \sum_{\mathbf{k}\in\mathscr{K}_{2d}} a_{\mathbf{k}}\Delta\boldsymbol{\theta}^{\mathbf{k}}, \tag{C.39a}$$

$$\det\left(\mathbf{M}(\Delta\boldsymbol{\theta})\right) = \sum_{\mathbf{k}\in\mathscr{K}_{2d}} b_{\mathbf{k}}\Delta\boldsymbol{\theta}^{\mathbf{k}}, \tag{C.39b}$$

where $d \geq n(L+1)$.

This definition results in

$$\det\left(\mathbf{M}(\Delta\boldsymbol{\theta})\right) - \det\left(\mathbf{H}_c(\Delta\boldsymbol{\theta})\right)\zeta = \sum_{\mathbf{k}\in\mathscr{K}_{2d}} \left(b_{\mathbf{k}} - a_{\mathbf{k}}\zeta\right)\Delta\boldsymbol{\theta}^{\mathbf{k}}. \tag{C.40}$$

Moreover,

$$\begin{aligned}\mathbf{v}_d(\Delta\boldsymbol{\theta})^{\mathrm{T}}\mathbf{Q}_0\mathbf{v}_d(\Delta\boldsymbol{\theta}) &= \operatorname{tr}\left(\mathbf{v}_d(\Delta\boldsymbol{\theta})\mathbf{v}_d(\Delta\boldsymbol{\theta})^{\mathrm{T}}\mathbf{Q}_0\right)\\ &= \sum_{\mathbf{k}\in\mathscr{K}_{2d}} \operatorname{tr}\left(\mathbf{R}_{0,\mathbf{k}}\mathbf{Q}_0\right)\Delta\boldsymbol{\theta}^{\mathbf{k}}\end{aligned} \tag{C.41}$$

and

$$\begin{aligned}\sum_{\mathbf{q}\in\mathscr{K}_2} c_{\mathbf{q}}\Delta\boldsymbol{\theta}^{\mathbf{q}}\mathbf{v}_{d-1}(\Delta\boldsymbol{\theta})^{\mathrm{T}}\mathbf{Q}_1\mathbf{v}_{d-1}(\Delta\boldsymbol{\theta}) &= \sum_{\mathbf{q}\in\mathscr{K}_2} c_{\mathbf{q}}\Delta\boldsymbol{\theta}^{\mathbf{q}}\operatorname{tr}\left(\mathbf{v}_{d-1}(\Delta\boldsymbol{\theta})\mathbf{v}_{d-1}(\Delta\boldsymbol{\theta})^{\mathrm{T}}\mathbf{Q}_1\right)\\ &= \sum_{\mathbf{q}\in\mathscr{K}_2} c_{\mathbf{q}}\Delta\boldsymbol{\theta}^{\mathbf{q}} \sum_{\substack{\mathbf{k}\in\mathscr{K}_{2d}\\ \mathbf{k}-\mathbf{q}\in\mathscr{K}_{2d}}} \operatorname{tr}\left(\mathbf{R}_{1,\mathbf{k}-\mathbf{q}}\mathbf{Q}_1\right)\Delta\boldsymbol{\theta}^{\mathbf{k}-\mathbf{q}}\\ &= \sum_{\mathbf{k}\in\mathscr{K}_{2d}} \sum_{\substack{\mathbf{q}\in\mathscr{K}_2\\ \mathbf{k}-\mathbf{q}\in\mathscr{K}_{2d}}} c_{\mathbf{q}}\operatorname{tr}\left(\mathbf{R}_{1,\mathbf{k}-\mathbf{q}}\mathbf{Q}_1\right)\Delta\boldsymbol{\theta}^{\mathbf{k}},\end{aligned} \tag{C.42}$$

which implies that it is equivalent to write

$$\begin{aligned}&\det\left(\mathbf{M}(\Delta\boldsymbol{\theta})\right) - \det\left(\mathbf{H}_c(\Delta\boldsymbol{\theta})\right)\zeta\\ &\quad= \mathbf{v}_d(\Delta\boldsymbol{\theta})^{\mathrm{T}}\mathbf{Q}_0\mathbf{v}_d(\Delta\boldsymbol{\theta}) + \sum_{\mathbf{q}\in\mathscr{K}_2} c_{\mathbf{q}}\Delta\boldsymbol{\theta}^{\mathbf{q}}\mathbf{v}_{d-1}(\Delta\boldsymbol{\theta})^{\mathrm{T}}\mathbf{Q}_1\mathbf{v}_{d-1}(\Delta\boldsymbol{\theta}), \quad \forall\Delta\boldsymbol{\theta},\end{aligned} \tag{C.43}$$

and

$$b_{\mathbf{k}} - a_{\mathbf{k}}\zeta = \operatorname{tr}\left(\mathbf{R}_{0,\mathbf{k}}\mathbf{Q}_0\right) + \sum_{\substack{\mathbf{q}\in\mathscr{K}_2\\ \mathbf{k}-\mathbf{q}\in\mathscr{K}_{2d}}} c_{\mathbf{q}}\operatorname{tr}\left(\mathbf{R}_{1,\mathbf{k}-\mathbf{q}}\mathbf{Q}_1\right), \quad \forall\mathbf{k}\in\mathscr{K}_{2d}. \tag{C.44}$$

From the equivalence of nonnegative polynomials and conical combination of sum-of-squares polynomials on a compact set, one can show that the feasibility of Eq. (C.38) is equivalent to the feasibility of a set of LMIs since the following three conditions are equiva-

lent:

$$\det\left(\mathbf{M}(\Delta\boldsymbol{\theta})\right) - \det\left(\mathbf{H}_c(\Delta\boldsymbol{\theta})\right)\zeta \geq 0,\ \forall \Delta\boldsymbol{\theta} \in \mathscr{C}, \tag{C.45}$$

$$\exists \mathbf{Q}_0, \mathbf{Q}_1 : \begin{cases} \mathbf{Q}_0 \succeq \mathbf{0}_{s(N,d)\times s(N,d)} \\ \mathbf{Q}_1 \succeq \mathbf{0}_{s(N,d-1)\times s(N,d-1)} \\ \det\left(\mathbf{M}(\Delta\boldsymbol{\theta})\right) - \det\left(\mathbf{H}_c(\Delta\boldsymbol{\theta})\right)\zeta \\ \quad = \mathbf{v}_d(\Delta\boldsymbol{\theta})^{\mathrm{T}}\mathbf{Q}_0\mathbf{v}_d(\Delta\boldsymbol{\theta}) + \sum\limits_{\mathbf{q}\in\mathscr{K}_2} c_{\mathbf{q}}\Delta\boldsymbol{\theta}^{\mathbf{q}}\mathbf{v}_{d-1}(\Delta\boldsymbol{\theta})^{\mathrm{T}}\mathbf{Q}_1\mathbf{v}_{d-1}(\Delta\boldsymbol{\theta}), \quad \forall\Delta\boldsymbol{\theta} \end{cases}, \tag{C.46}$$

$$\exists \mathbf{Q}_0, \mathbf{Q}_1 : \begin{cases} \mathbf{Q}_0 \succeq \mathbf{0}_{s(N,d)\times s(N,d)} \\ \mathbf{Q}_1 \succeq \mathbf{0}_{s(N,d-1)\times s(N,d-1)} \\ b_{\mathbf{k}} - a_{\mathbf{k}}\zeta = \mathrm{tr}\left(\mathbf{R}_{0,\mathbf{k}}\mathbf{Q}_0\right) + \sum\limits_{\substack{\mathbf{q}\in\mathscr{K}_2 \\ \mathbf{k}-\mathbf{q}\in\mathscr{K}_{2d}}} c_{\mathbf{q}}\,\mathrm{tr}\left(\mathbf{R}_{1,\mathbf{k}-\mathbf{q}}\mathbf{Q}_1\right), \quad \forall \mathbf{k} \in \mathscr{K}_{2d} \end{cases}. \tag{C.47}$$

Then, Eq. (C.45) is feasible if and only if there exist symmetric and positive semidefinite matrices $\mathbf{Q}_0$ and $\mathbf{Q}_1$ such that, for each $\mathbf{k} \in \mathscr{K}_{2d}$, $b_{\mathbf{k}} - a_{\mathbf{k}}\zeta$ is equal to a linear combination of the elements of $\mathbf{Q}_0$ and $\mathbf{Q}_1$ specified by the matrices $\mathbf{R}_{0,\mathbf{k}}$ and $\mathbf{R}_{1,\mathbf{k}-\mathbf{q}}$, for all $\mathbf{q} \in \mathscr{K}_2$ such that $\mathbf{k}-\mathbf{q} \in \mathscr{K}_{2d}$.

C.7 Computing the Solution $\Delta\boldsymbol{\theta}^*$

This proof shows that, for the primal problem, $\mathbf{v}_d(\Delta\boldsymbol{\theta}^*)$ lies in the null space of $\mathbf{Q}_0^*$, whereas for the dual problem, $\mathbf{v}_d(\Delta\boldsymbol{\theta}^*)$ lies in the row space of $\mathbf{L}_0^*$, where $\mathbf{L}_0$ is the dual variable of the LMI (C.34b). An algorithm that computes the solutions $\Delta\boldsymbol{\theta}^*$ using the knowledge of the space where $\mathbf{v}_d(\Delta\boldsymbol{\theta}^*)$ lies is described in [158].

C.7.1 Using the solution to the primal problem

One can note that $\Delta\boldsymbol{\theta}^*$ is indeed the global solution to the original problem if and only if

$$\begin{cases} \bar{J}_c(\Delta\boldsymbol{\theta}) - \zeta^* \geq 0,\ \forall\Delta\boldsymbol{\theta} \in \mathscr{C} \\ \bar{J}_c(\Delta\boldsymbol{\theta}^*) - \zeta^* = 0 \end{cases}, \tag{C.48}$$

which is equivalent to

$$\begin{cases} \det\left(\mathbf{M}(\Delta\boldsymbol{\theta})\right) - \det\left(\mathbf{H}_c(\Delta\boldsymbol{\theta})\right)\zeta^* \geq 0, \ \forall \Delta\boldsymbol{\theta} \in \mathscr{C} \\ \det\left(\mathbf{M}(\Delta\boldsymbol{\theta}^*)\right) - \det\left(\mathbf{H}_c(\Delta\boldsymbol{\theta}^*)\right)\zeta^* = 0 \end{cases}. \tag{C.49}$$

Since the solution $\mathbf{Q}_0^*, \mathbf{Q}_1^*$ of the SDP (C.34) must be feasible, the condition

$$\begin{cases} \mathbf{Q}_0^* \succeq \mathbf{0}_{s(N,d)\times s(N,d)} \\ \mathbf{Q}_1^* \succeq \mathbf{0}_{s(N,d-1)\times s(N,d-1)} \\ b_{\mathbf{k}} - a_{\mathbf{k}}\zeta^* = \operatorname{tr}\left(\mathbf{R}_{0,\mathbf{k}}\mathbf{Q}_0^*\right) + \sum\limits_{\substack{\mathbf{q}\in\mathscr{K}_2 \\ \mathbf{k}-\mathbf{q}\in\mathscr{K}_{2d}}} c_{\mathbf{q}} \operatorname{tr}\left(\mathbf{R}_{1,\mathbf{k}-\mathbf{q}}\mathbf{Q}_1^*\right), \quad \forall \mathbf{k} \in \mathscr{K}_{2d} \end{cases} \tag{C.50}$$

is satisfied, which, along with Eqs. (C.43) and (C.44), implies that

$$\begin{aligned} 0 &\leq \det\left(\mathbf{M}(\Delta\boldsymbol{\theta})\right) - \det\left(\mathbf{H}_c(\Delta\boldsymbol{\theta})\right)\zeta^* \\ &= \mathbf{v}_d(\Delta\boldsymbol{\theta})^{\mathrm{T}}\mathbf{Q}_0^*\mathbf{v}_d(\Delta\boldsymbol{\theta}) + \sum_{\mathbf{q}\in\mathscr{K}_2} c_{\mathbf{q}}\Delta\boldsymbol{\theta}^{\mathbf{q}}\mathbf{v}_{d-1}(\Delta\boldsymbol{\theta})^{\mathrm{T}}\mathbf{Q}_1^*\mathbf{v}_{d-1}(\Delta\boldsymbol{\theta}), \ \forall \Delta\boldsymbol{\theta} \in \mathscr{C}. \end{aligned} \tag{C.51}$$

Hence, from Eqs. (C.48) and (C.51), a sufficient and necessary condition to find $\Delta\boldsymbol{\theta}^* \in \mathscr{C}$ is

$$\mathbf{v}_d(\Delta\boldsymbol{\theta}^*)^{\mathrm{T}}\mathbf{Q}_0^*\mathbf{v}_d(\Delta\boldsymbol{\theta}^*) + \sum_{\mathbf{q}\in\mathscr{K}_2} c_{\mathbf{q}}\Delta\boldsymbol{\theta}^{*\mathbf{q}}\mathbf{v}_{d-1}(\Delta\boldsymbol{\theta}^*)^{\mathrm{T}}\mathbf{Q}_1^*\mathbf{v}_{d-1}(\Delta\boldsymbol{\theta}^*) = 0. \tag{C.52}$$

From Eqs. (C.50) and (C.52), one can see that

$$\begin{cases} \mathbf{Q}_0^* \succeq \mathbf{0}_{s(N,d)\times s(N,d)} \\ \mathbf{v}_d(\Delta\boldsymbol{\theta}^*)^{\mathrm{T}}\mathbf{Q}_0^*\mathbf{v}_d(\Delta\boldsymbol{\theta}^*) = 0 \end{cases}, \tag{C.53}$$

which implies that $\mathbf{Q}_0^*$ has at least one eigenvalue equal to 0, while all the other eigenvalues are positive.

From the eigenvalue decomposition

$$\mathbf{Q}_0^* = \sum_{l=1}^{s(N,d)} \lambda_l \mathbf{u}_l \mathbf{u}_l^{\mathrm{T}} \tag{C.54}$$

and Eq. (C.53), one can see that

$$0 = \mathbf{v}_d(\Delta\boldsymbol{\theta}^*)^{\mathrm{T}}\mathbf{Q}_0^*\mathbf{v}_d(\Delta\boldsymbol{\theta}^*) = \sum_{l=1}^{s(N,d)} \lambda_l \left(\mathbf{u}_l^{\mathrm{T}}\mathbf{v}_d(\Delta\boldsymbol{\theta}^*)\right)^2, \tag{C.55}$$

therefore $\Delta\boldsymbol{\theta}^*$ must be such that $\mathbf{v}_d(\Delta\boldsymbol{\theta}^*)$ lies in the null space of $\mathbf{Q}_0^*$.

C.7.2 Using the solution to the dual problem

Since the Lagrangian of Problem (C.34) is

$$\mathscr{L}(\zeta, \mathbf{Q}_0, \mathbf{Q}_1, \mathbf{L}_0, \mathbf{L}_1, \boldsymbol{\mu}) = \begin{cases} \zeta + \operatorname{tr}(\mathbf{L}_0\mathbf{Q}_0) + \operatorname{tr}(\mathbf{L}_1\mathbf{Q}_1) + \sum_{\mathbf{k}\in\mathscr{K}_{2d}} \left(b_\mathbf{k} - a_\mathbf{k}\zeta\right)\mu_\mathbf{k} \\ -\left(\sum_{\mathbf{k}\in\mathscr{K}_{2d}} \operatorname{tr}\left(\mathbf{R}_{0,\mathbf{k}}\mathbf{Q}_0\right)\mu_\mathbf{k}\right) \\ -\left(\sum_{\mathbf{k}\in\mathscr{K}_{2d}} \sum_{\substack{\mathbf{q}\in\mathscr{K}_2 \\ \mathbf{k}-\mathbf{q}\in\mathscr{K}_{2d}}} c_\mathbf{q} \operatorname{tr}\left(\mathbf{R}_{1,\mathbf{k}-\mathbf{q}}\mathbf{Q}_1\right)\mu_\mathbf{k}\right), & \text{if } \begin{cases} \mathbf{L}_0 \succeq \mathbf{0}_{s(N,d)\times s(N,d)} \\ \mathbf{L}_1 \succeq \mathbf{0}_{s(N,d-1)\times s(N,d-1)} \end{cases}, \\ \infty, & \text{otherwise} \end{cases} \tag{C.56}$$

the dual of that problem is

$$\begin{aligned} &\min_{\mathbf{L}_0,\mathbf{L}_1,\boldsymbol{\mu}} \quad \max_{\zeta,\mathbf{Q}_0,\mathbf{Q}_1} \quad \mathscr{L}(\zeta, \mathbf{Q}_0, \mathbf{Q}_1, \mathbf{L}_0, \mathbf{L}_1, \boldsymbol{\mu}) \\ &= \min_{\mathbf{L}_0,\mathbf{L}_1,\boldsymbol{\mu}} \quad \sum_{\mathbf{k}\in\mathscr{K}_{2d}} b_\mathbf{k}\mu_\mathbf{k} && \text{(C.57a)} \\ &\qquad \text{s.t.} \quad 1 = \sum_{\mathbf{k}\in\mathscr{K}_{2d}} a_\mathbf{k}\mu_\mathbf{k} && \text{(C.57b)} \\ &\qquad\quad \mathbf{L}_0 \succeq \mathbf{0}_{s(N,d)\times s(N,d)} && \text{(C.57c)} \\ &\qquad\quad \mathbf{L}_1 \succeq \mathbf{0}_{s(N,d-1)\times s(N,d-1)} && \text{(C.57d)} \\ &\qquad\quad \mathbf{L}_0 = \sum_{\mathbf{k}\in\mathscr{K}_{2d}} \mathbf{R}_{0,\mathbf{k}}\mu_\mathbf{k} && \text{(C.57e)} \\ &\qquad\quad \mathbf{L}_1 = \sum_{\mathbf{k}\in\mathscr{K}_{2d}} \sum_{\substack{\mathbf{q}\in\mathscr{K}_2 \\ \mathbf{k}-\mathbf{q}\in\mathscr{K}_{2d}}} c_\mathbf{q}\mathbf{R}_{1,\mathbf{k}-\mathbf{q}}\mu_\mathbf{k}. && \text{(C.57f)} \end{aligned}$$

In the dual Problem (C.57), $\mathbf{L}_0$ is the dual variable of the LMI (C.34b), $\mathbf{L}_1$ is the dual variable of the LMI (C.34c) and $\mu_\mathbf{k}$ is the dual variable of the equality constraint in Eq. (C.34d), $\forall \mathbf{k} \in \mathscr{K}_{2d}$.

Since both the primal Problem (C.34) and the dual Problem (C.57) are convex SDPs, strong duality holds and the optimal value of the objective function is equal in both cases, which implies that the solution $\boldsymbol{\mu}^*$ must satisfy

$$\zeta^* = \sum_{\mathbf{k}\in\mathscr{K}_{2d}} b_\mathbf{k}\mu_\mathbf{k}^*. \tag{C.58}$$

Let us assume that $\Delta\boldsymbol{\theta}^*(1), \ldots, \Delta\boldsymbol{\theta}^*(G)$ are the G global solutions to Problem (4.77).

Note that, for all $l = 1, \ldots, G$, there exist $\rho_l > 0$ such that

$$\begin{cases} \sum_{\mathbf{k} \in \mathscr{K}_{2d}} \left(b_{\mathbf{k}} - a_{\mathbf{k}} \zeta^*\right) \sum_{l=1}^{G} \rho_l \Delta\boldsymbol{\theta}^*(l)^{\mathbf{k}} = 0 \\ \sum_{\mathbf{k} \in \mathscr{K}_{2d}} a_{\mathbf{k}} \sum_{l=1}^{G} \rho_l \Delta\boldsymbol{\theta}^*(l)^{\mathbf{k}} > 0 \end{cases}, \tag{C.59}$$

otherwise ζ^* would not be the optimum of the primal Problem (C.34). Then, it is possible to show that $\boldsymbol{\mu}^*$ is a solution to the dual Problem (C.57) if it is such that

$$\mu^*_{\mathbf{k}} = \sum_{l=1}^{G} \lambda_l \Delta\boldsymbol{\theta}^*(l)^{\mathbf{k}}, \qquad \forall \mathbf{k} \in \mathscr{K}_{2d}, \tag{C.60}$$

where

$$\lambda_l = \frac{\rho_l}{\sum_{\mathbf{k} \in \mathscr{K}_{2d}} a_{\mathbf{k}} \sum_{l=1}^{G} \rho_l \Delta\boldsymbol{\theta}^*(l)^{\mathbf{k}}} > 0, \qquad \forall l = 1, \ldots, G. \tag{C.61}$$

This implies that

$$\sum_{\mathbf{k} \in \mathscr{K}_{2d}} a_{\mathbf{k}} \mu^*_{\mathbf{k}} = \sum_{\mathbf{k} \in \mathscr{K}_{2d}} a_{\mathbf{k}} \frac{\sum_{l=1}^{G} \rho_l \Delta\boldsymbol{\theta}^*(l)^{\mathbf{k}}}{\sum_{\mathbf{k} \in \mathscr{K}_{2d}} a_{\mathbf{k}} \sum_{l=1}^{G} \rho_l \Delta\boldsymbol{\theta}^*(l)^{\mathbf{k}}} = 1 \tag{C.62}$$

and

$$\zeta^* = \sum_{\mathbf{k} \in \mathscr{K}_{2d}} a_{\mathbf{k}} \zeta^* \mu^*_{\mathbf{k}}. \tag{C.63}$$

Note that, according to Eqs. (C.60) and (C.63), the solution $\boldsymbol{\mu}^*$ satisfies

$$\begin{aligned} \sum_{\mathbf{k} \in \mathscr{K}_{2d}} b_{\mathbf{k}} \mu^*_{\mathbf{k}} - \zeta^* &= \sum_{\mathbf{k} \in \mathscr{K}_{2d}} \left(b_{\mathbf{k}} - a_{\mathbf{k}} \zeta^*\right) \mu^*_{\mathbf{k}} \\ &= \sum_{\mathbf{k} \in \mathscr{K}_{2d}} \left(b_{\mathbf{k}} - a_{\mathbf{k}} \zeta^*\right) \sum_{l=1}^{G} \lambda_l \Delta\boldsymbol{\theta}^*(l)^{\mathbf{k}} \\ &= 0, \end{aligned} \tag{C.64}$$

and this solution yields the optimal value of the objective function shown in Eq. (C.58).

Finally, one can show that the remaining constraints are also satisfied by the solution $\boldsymbol{\mu}^*$

because, in that case, one can set

$$\begin{aligned}\mathbf{L}_0^* &= \sum_{\mathbf{k}\in\mathscr{K}_{2d}} \mathbf{R}_{0,\mathbf{k}} \sum_{l=1}^{G} \lambda_l \Delta\boldsymbol{\theta}^*(l)^{\mathbf{k}} \\ &= \sum_{l=1}^{G} \lambda_l \sum_{\mathbf{k}\in\mathscr{K}_{2d}} \mathbf{R}_{0,\mathbf{k}} \Delta\boldsymbol{\theta}^*(l)^{\mathbf{k}} \\ &= \sum_{l=1}^{G} \lambda_l \mathbf{v}_d(\Delta\boldsymbol{\theta}^*(l))\mathbf{v}_d(\Delta\boldsymbol{\theta}^*(l))^{\mathrm{T}}, \end{aligned} \tag{C.65a}$$

$$\begin{aligned}\mathbf{L}_1^* &= \sum_{\mathbf{k}\in\mathscr{K}_{2d}} \sum_{\substack{\mathbf{q}\in\mathscr{K}_2 \\ \mathbf{k}-\mathbf{q}\in\mathscr{K}_{2d}}} c_{\mathbf{q}} \mathbf{R}_{1,\mathbf{k}-\mathbf{q}} \sum_{l=1}^{G} \lambda_l \Delta\boldsymbol{\theta}^*(l)^{\mathbf{k}} \\ &= \sum_{l=1}^{G} \lambda_l \sum_{\mathbf{q}\in\mathscr{K}_2} c_{\mathbf{q}} \Delta\boldsymbol{\theta}^*(l)^{\mathbf{q}} \sum_{\substack{\mathbf{k}\in\mathscr{K}_{2d} \\ \mathbf{k}-\mathbf{q}\in\mathscr{K}_{2d}}} \mathbf{R}_{1,\mathbf{k}-\mathbf{q}} \Delta\boldsymbol{\theta}^*(l)^{\mathbf{k}-\mathbf{q}} \\ &= \sum_{l=1}^{G} \lambda_l \sum_{\mathbf{q}\in\mathscr{K}_2} c_{\mathbf{q}} \Delta\boldsymbol{\theta}^*(l)^{\mathbf{q}} \mathbf{v}_{d-1}(\Delta\boldsymbol{\theta}^*(l))\mathbf{v}_{d-1}(\Delta\boldsymbol{\theta}^*(l))^{\mathrm{T}}, \end{aligned} \tag{C.65b}$$

which satisfies the constraints

$$\begin{cases} \mathbf{L}_0^* \succeq \mathbf{0}_{s(N,d)\times s(N,d)} \\ \mathbf{L}_1^* \succeq \mathbf{0}_{s(N,d-1)\times s(N,d-1)} \\ \mathbf{L}_0^* = \displaystyle\sum_{\mathbf{k}\in\mathscr{K}_{2d}} \mathbf{R}_{0,\mathbf{k}} \mu_{\mathbf{k}}^* \\ \mathbf{L}_1^* = \displaystyle\sum_{\mathbf{k}\in\mathscr{K}_{2d}} \sum_{\substack{\mathbf{q}\in\mathscr{K}_2 \\ \mathbf{k}-\mathbf{q}\in\mathscr{K}_{2d}}} c_{\mathbf{q}} \mathbf{R}_{1,\mathbf{k}-\mathbf{q}} \mu_{\mathbf{k}}^* \end{cases}. \tag{C.66}$$

From Eq. (C.65a), it is possible to observe that, for each solution $\Delta\boldsymbol{\theta}^*$, $\mathbf{v}_d(\Delta\boldsymbol{\theta}^*)$ lies in the space spanned by the eigenvectors of $\mathbf{L}_0^*$ that correspond to its positive eigenvalues, that is, the row space of $\mathbf{L}_0^*$.

C.8 Unbiased Rate Estimation via the Convex Extent-based Incremental Approach

Let us show that, if Eq. (4.79) is satisfied and all the measurements $\tilde{\mathbf{z}}(t)$ needed to compute $\hat{r}_{\ell,\mathbf{k}}\big(\tilde{\mathbf{z}}(t)\big)$ are uncorrelated and corrupted by zero-mean noise, then $\hat{r}_{\ell,\mathbf{k}}\big(\tilde{\mathbf{z}}(t)\big)$ is an unbiased estimate of $\frac{\partial^{\mathbf{k}} r_\ell}{\partial \boldsymbol{\theta}^{\mathbf{k}}}\big(\mathbf{z}(t), \bar{\boldsymbol{\theta}}\big)$, and Eq. (4.80) holds.

According to Section 4.3.2, $\hat{r}_{\ell,\mathbf{k},j,s}\big(\tilde{z}_s(t)\big)$ can be assumed to be an unbiased estimate

of $r_{\ell,\mathbf{k},j,s}\big(z_s(t)\big)$ for all $s = 1,\dots,S+1$ if $\tilde{z}_s(t)$ is corrupted by zero-mean noise. Hence, if Eq. (4.79) is satisfied and all the measurements $\tilde{\mathbf{z}}(t)$ needed to compute $\hat{r}_{\ell,\mathbf{k}}\big(\tilde{\mathbf{z}}(t)\big)$ are uncorrelated and corrupted by zero-mean noise, then

$$\begin{aligned}
\mathrm{E}\left[\hat{r}_{\ell,\mathbf{k}}\big(\tilde{\mathbf{z}}(t)\big)\right] &= \mathrm{E}\left[\sum_{j=1}^{J} w_{\ell,\mathbf{k},j} \prod_{s=1}^{S+1} \hat{r}_{\ell,\mathbf{k},j,s}\big(\tilde{z}_s(t)\big)\right] \\
&= \sum_{j=1}^{J} w_{\ell,\mathbf{k},j} \prod_{s=1}^{S+1} \mathrm{E}\left[\hat{r}_{\ell,\mathbf{k},j,s}\big(\tilde{z}_s(t)\big)\right] \\
&= \sum_{j=1}^{J} w_{\ell,\mathbf{k},j} \prod_{s=1}^{S+1} r_{\ell,\mathbf{k},j,s}\big(z_s(t)\big) \\
&= \frac{\partial^{\mathbf{k}} r_\ell}{\partial \boldsymbol{\theta}^{\mathbf{k}}}\big(\mathbf{z}(t), \bar{\boldsymbol{\theta}}\big), \qquad \forall \ell = 0,\dots,L, \qquad \forall \mathbf{k} \in \mathscr{K}_n,
\end{aligned} \tag{C.67}$$

which shows that $\hat{r}_{\ell,\mathbf{k}}\big(\tilde{\mathbf{z}}(t)\big)$ is indeed an unbiased estimate of $\frac{\partial^{\mathbf{k}} r_\ell}{\partial \boldsymbol{\theta}^{\mathbf{k}}}\big(\mathbf{z}(t), \bar{\boldsymbol{\theta}}\big)$.

Then, similarly to Eqs. (C.30) and (C.31), one can show that

$$\lim_{h\to 0} \mathrm{E}\left[\hat{d}_{\ell,\mathbf{k}}(t)\right] = d_{\ell,\mathbf{k}}(t), \qquad \forall \ell = 0,\dots,L, \qquad \forall \mathbf{k} \in \mathscr{K}_n, \tag{C.68}$$

and, if the measurements at different time instants are uncorrelated,

$$\lim_{h\to 0} \mathrm{Var}\left[\hat{d}_{\ell,\mathbf{k}}(t)\right] = 0, \qquad \forall \ell = 0,\dots,L, \qquad \forall \mathbf{k} \in \mathscr{K}_n, \tag{C.69}$$

which implies that Eq. (4.80) holds.

D Appendix of Chapter 5

D.1 Numerical Differentiation Using the Savitzky-Golay Filter

Proposition D.1. *Let $\mathbf{y}^{(n-1)}$ be Lipschitz continuous, and let $\mathscr{S}_{p,n,q,w}(\tilde{\mathbf{y}},t)$ be the p-th differentiation Savitzky-Golay filter [109] of order n and odd window size $q>1$ given for the point $w+1$ of the window and applied to the noisy function $\tilde{\mathbf{y}}$ on the interval $[t-\Delta t,t]$, with $\Delta t := (q-1)\,h$. If $\mathscr{S}_{p,n,q,w}(\tilde{\mathbf{y}},t)$ is defined as*

$$\mathscr{S}_{p,n,q,w}(\tilde{\mathbf{y}},t) := \frac{p!}{h^p}\sum_{k=0}^{q-1}\left(\mathbf{c}_{p,n,w}\right)_{k+1}\tilde{\mathbf{y}}(t-\Delta t+kh), \tag{D.1}$$

where

$$\begin{aligned}\left(\mathbf{c}_{p,n,w}\right)_{k+1} &= \sum_{m=p}^{n}\binom{m}{p}\left(w-\tfrac{q-1}{2}\right)^{m-p}\left(\mathbf{C}_n\right)_{k+1,m+1}\\ &= \sum_{i=0}^{n}\left(k-\tfrac{q-1}{2}\right)^{i}\left(\mathbf{a}_{p,n,w}\right)_{i+1}, \qquad k=0,\dots,q-1,\end{aligned} \tag{D.2}$$

with

$$\left(\mathbf{C}_n\right)_{k+1,m+1} = \sum_{i=0}^{n}\left(k-\tfrac{q-1}{2}\right)^{i}\left(\mathbf{A}_n\right)_{i+1,m+1}, \qquad k=0,\dots,q-1, \qquad m=0,\dots,n, \tag{D.3}$$

$$\left(\mathbf{a}_{p,n,w}\right)_{i+1} = \sum_{m=p}^{n}\binom{m}{p}\left(w-\tfrac{q-1}{2}\right)^{m-p}\left(\mathbf{A}_n\right)_{i+1,m+1}, \qquad i=0,\dots,n, \tag{D.4}$$

where $\mathbf{A}_n$ is the unique solution to

$$\mathbf{G}_n\mathbf{A}_n = \mathbf{I}_{n+1}, \tag{D.5}$$

with

$$\left(\mathbf{G}_n\right)_{l+1,i+1} = \sum_{k=0}^{q-1} \left(k - \tfrac{q-1}{2}\right)^{i+l}, \qquad l = 0,\dots,n, \qquad i = 0,\dots,n, \tag{D.6}$$

then the expected value of $\mathscr{S}_{p,n,q,w}(\tilde{\mathbf{y}}, t)$ *is given by*

$$\begin{aligned}
&\mathrm{E}\left[\mathscr{S}_{p,n,q,w}(\tilde{\mathbf{y}}, t)\right] \\
&= \mathbf{y}^{(p)}(t - \Delta t + wh) \\
&\quad - \frac{p!}{h^p}\left(\sum_{k=0}^{q-1}\left(\mathbf{c}_{p,n,w}\right)_{k+1} \int_w^k \frac{\mathbf{y}^{(n)}(t-\Delta t+wh) - \mathbf{y}^{(n)}(t-\Delta t+\xi h)}{(n-1)!} h^n (k-\xi)^{n-1}\,\mathrm{d}\xi\right),
\end{aligned} \tag{D.7}$$

while the covariance of $\sum_{m=1}^{H} \lambda_1^{m-1} \frac{h^p}{p!} \mathscr{S}_{p,n,q,w}(\mathbf{d}_{\mathbf{y}}, t - mh)$ *and* $\sum_{m=1}^{H} \lambda_2^{m-1} \frac{h^p}{p!} \mathscr{S}_{p,n,q,w}(\mathbf{d}_{\mathbf{y}}, t - mh)$ *and the covariance of* $\sum_{m=1}^{H} \lambda_1^{m-1} h \mathbf{d}_{\mathbf{x}}(t - mh)$ *and* $\sum_{m=1}^{H} \lambda_2^{m-1} \frac{h^p}{p!} \mathscr{S}_{p,n,q,w}(\mathbf{d}_{\mathbf{y}}, t - mh)$*, where* $-1 < \lambda_1 < 1$ *and* $-1 < \lambda_2 < 1$*, are given by*

$$\begin{aligned}
&\mathrm{Cov}\left[\sum_{m=1}^{H} \lambda_1^{m-1} \frac{h^p}{p!} \mathscr{S}_{p,n,q,w}(\mathbf{d}_{\mathbf{y}}, t - mh), \sum_{m=1}^{H} \lambda_2^{m-1} \frac{h^p}{p!} \mathscr{S}_{p,n,q,w}(\mathbf{d}_{\mathbf{y}}, t - mh)\right] \\
&= \mathrm{Var}\left[\mathbf{d}_{\mathbf{y}}(t)\right] \frac{\beta'_{p,n,q,w}(\lambda_1, \lambda_2, H)}{1 - \lambda_1\lambda_2},
\end{aligned} \tag{D.8}$$

$$\begin{aligned}
&\mathrm{Cov}\left[\sum_{m=1}^{H} \lambda_1^{m-1} h \mathbf{d}_{\mathbf{x}}(t - mh), \sum_{m=1}^{H} \lambda_2^{m-1} \frac{h^p}{p!} \mathscr{S}_{p,n,q,w}(\mathbf{d}_{\mathbf{y}}, t - mh)\right] \\
&= \mathrm{Cov}\left[\mathbf{d}_{\mathbf{x}}(t), \mathbf{d}_{\mathbf{y}}(t)\right] \frac{h\gamma'_{p,n,q,w}(\lambda_1, \lambda_2, H)}{1 - \lambda_1\lambda_2},
\end{aligned} \tag{D.9}$$

with

$$\begin{aligned}
\beta'_{p,n,q,w}(\lambda_1, \lambda_2, H) = &\sum_{l=1}^{\min(H,q-1)} \lambda_2^l \left(1 - (\lambda_1\lambda_2)^{H-l}\right) \sum_{k=l}^{q-1} \left(\mathbf{c}_{p,n,w}\right)_{k+1} \left(\mathbf{c}_{p,n,w}\right)_{k-l+1} \\
&+ \sum_{l=1}^{\min(H,q-1)} \lambda_1^l \left(1 - (\lambda_1\lambda_2)^{H-l}\right) \sum_{k=l}^{q-1} \left(\mathbf{c}_{p,n,w}\right)_{k+1} \left(\mathbf{c}_{p,n,w}\right)_{k-l+1} \\
&+ \left(1 - (\lambda_1\lambda_2)^{H}\right) \sum_{k=0}^{q-1} \left(\mathbf{c}_{p,n,w}\right)_{k+1}^2,
\end{aligned} \tag{D.10}$$

$$\gamma'_{p,n,q,w}(\lambda_1, \lambda_2, H) = \sum_{k=\max(q-1-H,0)}^{q-1} \left(\lambda_1^{-(k-q+1)} \left(1 - (\lambda_1\lambda_2)^{H+k-q+1}\right)\right) \left(\mathbf{c}_{p,n,w}\right)_{k+1}, \tag{D.11}$$

provided that the measurements $\tilde{\mathbf{y}}(t)$ are corrupted by zero-mean noise, and the measurements $\tilde{\mathbf{y}}(t-mh)$ and $\tilde{\mathbf{x}}(t-mh)$ at different time instants, for $m=1,\ldots,H$, where H is an arbitrary number of sampling times, are independent and identically distributed.

Proof. Note that the definition of $\mathbf{C}_n$ implies that

$$\begin{aligned}\sum_{k=0}^{q-1}\left(k-\tfrac{q-1}{2}\right)^{l}\left(\mathbf{C}_n\right)_{k+1,m+1} &= \sum_{i=0}^{n}\sum_{k=0}^{q-1}\left(k-\tfrac{q-1}{2}\right)^{i+l}\left(\mathbf{A}_n\right)_{i+1,m+1}\\ &= \sum_{i=0}^{n}\left(\mathbf{G}_n\right)_{l+1,i+1}\left(\mathbf{A}_n\right)_{i+1,m+1}\\ &= \begin{cases}0, & l\neq m\\ 1, & l=m\end{cases}, \qquad l=0,\ldots,n, \qquad m=0,\ldots,n.\end{aligned} \tag{D.12}$$

The previous equality results in

$$
\begin{aligned}
&\sum_{k=0}^{q-1}(k-w)^l\left(\mathbf{c}_{p,n,w}\right)_{k+1}\\
&=\sum_{k=0}^{q-1}(k-w)^l\left(\sum_{m=p}^{n}\tbinom{m}{p}\left(w-\tfrac{q-1}{2}\right)^{m-p}\left(\mathbf{C}_n\right)_{k+1,m+1}\right)\\
&=\sum_{k=0}^{q-1}\sum_{m=p}^{n}\tbinom{m}{p}\left(w-\tfrac{q-1}{2}\right)^{m-p}\left(\mathbf{C}_n\right)_{k+1,m+1}\left(\sum_{j=0}^{l}\tbinom{l}{j}\left(k-\tfrac{q-1}{2}\right)^{j}\left(\tfrac{q-1}{2}-w\right)^{l-j}\right)\\
&=\sum_{m=p}^{n}\tbinom{m}{p}\left(w-\tfrac{q-1}{2}\right)^{m-p}\left(\sum_{j=0}^{l}\tbinom{l}{j}\left(\tfrac{q-1}{2}-w\right)^{l-j}\left(\sum_{k=0}^{q-1}\left(k-\tfrac{q-1}{2}\right)^{j}\left(\mathbf{C}_n\right)_{k+1,m+1}\right)\right)\\
&=\begin{cases}0, & l=0,\dots,p-1\\ \sum_{m=p}^{l}\tbinom{m}{p}\left(w-\frac{q-1}{2}\right)^{m-p}\tbinom{l}{m}\left(\frac{q-1}{2}-w\right)^{l-m}, & l=p,\dots,n\end{cases}\\
&=\begin{cases}0, & l=0,\dots,p-1\\ \sum_{m=0}^{l-p}\tbinom{m+p}{p}\left(w-\frac{q-1}{2}\right)^{m}\tbinom{l}{m+p}\left(\frac{q-1}{2}-w\right)^{l-p-m}, & l=p,\dots,n\end{cases}\\
&=\begin{cases}0, & l=0,\dots,p-1\\ \frac{l!}{p!(l-p)!}\sum_{m=0}^{l-p}\frac{(l-p)!}{m!(l-p-m)!}\left(w-\frac{q-1}{2}\right)^{m}\left(\frac{q-1}{2}-w\right)^{l-p-m}, & l=p,\dots,n\end{cases}\\
&=\begin{cases}0, & l=0,\dots,p-1\\ \frac{l!}{p!(l-p)!}0^{l-p}, & l=p,\dots,n\end{cases}\\
&=\begin{cases}0, & l\neq p\\ 1, & l=p\end{cases}, \qquad l=0,\dots,n. \qquad \text{(D.13)}
\end{aligned}
$$

Consequently,

$$\begin{aligned}\sum_{k=0}^{q-1}\left(\mathbf{c}_{p,n,w}\right)_{k+1}\int_w^k p!\frac{(k-\xi)^{n-1}}{(n-1)!}\mathrm{d}\xi &= \frac{p!}{(n-1)!}\left(\sum_{k=0}^{q-1}\left(\mathbf{c}_{p,n,w}\right)_{k+1}\left[-\frac{(k-\xi)^n}{n}\right]_w^k\right)\\ &= \frac{p!}{n!}\left(\sum_{k=0}^{q-1}(k-w)^n\left(\mathbf{c}_{p,n,w}\right)_{k+1}\right)\\ &= \begin{cases}0, & n\neq p\\ 1, & n=p\end{cases}. \end{aligned} \tag{D.14}$$

From the fact that the measurements $\tilde{\mathbf{y}}(t)$ are corrupted by zero-mean noise and the fact that $\mathbf{y}^{(n-1)}$ is Lipschitz continuous, the expected value of $\mathscr{S}_{p,n,q,w}(\tilde{\mathbf{y}},t)$ is

$$\begin{aligned}&\mathrm{E}\left[\mathscr{S}_{p,n,q,w}(\tilde{\mathbf{y}},t)\right]\\ &=\mathscr{S}_{p,n,q,w}(\mathbf{y},t)\\ &=\frac{p!}{h^p}\sum_{k=0}^{q-1}\left(\mathbf{c}_{p,n,w}\right)_{k+1}\mathbf{y}(t-\Delta t+kh)\\ &=\frac{p!}{h^p}\left(\sum_{k=0}^{q-1}\left(\mathbf{c}_{p,n,w}\right)_{k+1}\left(\sum_{l=0}^{n-1}\frac{\mathbf{y}^{(l)}(t-\Delta t+wh)}{l!}\left((k-w)h\right)^l\right)\right)\\ &\quad+\frac{p!}{h^p}\left(\sum_{k=0}^{q-1}\left(\mathbf{c}_{p,n,w}\right)_{k+1}\int_{wh}^{kh}\frac{\mathbf{y}^{(n)}(t-\Delta t+\tau)}{(n-1)!}\left(kh-\tau\right)^{n-1}\mathrm{d}\tau\right)\\ &=\sum_{l=0}^{n-1}\mathbf{y}^{(l)}(t-\Delta t+wh)\frac{p!h^{l-p}}{l!}\left(\sum_{k=0}^{q-1}(k-w)^l\left(\mathbf{c}_{p,n,w}\right)_{k+1}\right)\\ &\quad+h^{-p}\left(\sum_{k=0}^{q-1}\left(\mathbf{c}_{p,n,w}\right)_{k+1}\int_w^k p!\mathbf{y}^{(n)}(t-\Delta t+\xi h)h^n\tfrac{(k-\xi)^{n-1}}{(n-1)!}\mathrm{d}\xi\right),\end{aligned} \tag{D.15}$$

which implies that, for $p=0,\ldots,n-1$,

$$\begin{aligned}&\mathrm{E}\left[\mathscr{S}_{p,n,q,w}(\tilde{\mathbf{y}},t)\right]\\ &=\mathscr{S}_{p,n,q,w}(\mathbf{y},t)\\ &=\mathbf{y}^{(p)}(t-\Delta t+wh)+h^{-p}\left(\sum_{k=0}^{q-1}\left(\mathbf{c}_{p,n,w}\right)_{k+1}\int_w^k p!\mathbf{y}^{(n)}(t-\Delta t+\xi h)h^n\tfrac{(k-\xi)^{n-1}}{(n-1)!}\mathrm{d}\xi\right)\\ &=\mathbf{y}^{(p)}(t-\Delta t+wh)\\ &\quad-\frac{p!}{h^p}\left(\sum_{k=0}^{q-1}\left(\mathbf{c}_{p,n,w}\right)_{k+1}\int_w^k\frac{\mathbf{y}^{(n)}(t-\Delta t+wh)-\mathbf{y}^{(n)}(t-\Delta t+\xi h)}{(n-1)!}h^n\left(k-\xi\right)^{n-1}\mathrm{d}\xi\right),\end{aligned} \tag{D.16}$$

and

$$\begin{aligned}
&\mathrm{E}\left[\mathscr{S}_{p,p,q,w}(\tilde{\mathbf{y}},t)\right]\\
&=\mathscr{S}_{p,p,q,w}(\mathbf{y},t)\\
&=h^{-p}\left(\sum_{k=0}^{q-1}\left(\mathbf{c}_{p,p,w}\right)_{k+1}\int_w^k p!\mathbf{y}^{(p)}(t-\Delta t+\xi h)h^p\frac{(k-\xi)^{p-1}}{(p-1)!}\mathrm{d}\xi\right)\\
&=\mathbf{y}^{(p)}(t-\Delta t+wh)\\
&\qquad-\frac{p!}{h^p}\left(\sum_{k=0}^{q-1}\left(\mathbf{c}_{p,p,w}\right)_{k+1}\int_w^k\frac{\mathbf{y}^{(p)}(t-\Delta t+wh)-\mathbf{y}^{(p)}(t-\Delta t+\xi h)}{(p-1)!}h^p\,(k-\xi)^{p-1}\,\mathrm{d}\xi\right).
\end{aligned}\tag{D.17}$$

The fact that the measurements $\tilde{\mathbf{y}}(t-mh)$ and $\tilde{\mathbf{x}}(t-mh)$ at different time instants, for $m=0,\ldots,H$, are independent and identically distributed results in the covariance of

$\sum_{m=1}^{H} \lambda_1^{m-1} \frac{h^p}{p!} \mathscr{S}_{p,n,q,w}(\mathbf{d}_\mathbf{y}, t-mh)$ and $\sum_{m=1}^{H} \lambda_2^{m-1} \frac{h^p}{p!} \mathscr{S}_{p,n,q,w}(\mathbf{d}_\mathbf{y}, t-mh)$

$$
\begin{aligned}
&\operatorname{Cov}\left[\sum_{m=1}^{H} \lambda_1^{m-1} \frac{h^p}{p!} \mathscr{S}_{p,n,q,w}(\mathbf{d}_\mathbf{y}, t-mh), \sum_{m=1}^{H} \lambda_2^{m-1} \frac{h^p}{p!} \mathscr{S}_{p,n,q,w}(\mathbf{d}_\mathbf{y}, t-mh)\right] \\
&= \operatorname{Cov}\left[\sum_{m=1}^{H} \lambda_1^{m-1} \left(\sum_{k=0}^{q-1} \left(\mathbf{c}_{p,n,w}\right)_{k+1} \mathbf{d}_\mathbf{y}(t-mh-\Delta t+kh)\right),\right. \\
&\qquad \left.\sum_{m=1}^{H} \lambda_2^{m-1} \left(\sum_{k=0}^{q-1} \left(\mathbf{c}_{p,n,w}\right)_{k+1} \mathbf{d}_\mathbf{y}(t-mh-\Delta t+kh)\right)\right] \\
&= \operatorname{Cov}\left[\sum_{m=1}^{H} \lambda_1^{m-1} \left(\sum_{k=0}^{q-1} \left(\mathbf{c}_{p,n,w}\right)_{k+1} \mathbf{d}_\mathbf{y}(t-\Delta t+(k-m)h)\right),\right. \\
&\qquad \left.\sum_{m=1}^{H} \lambda_2^{m-1} \left(\sum_{k=0}^{q-1} \left(\mathbf{c}_{p,n,w}\right)_{k+1} \mathbf{d}_\mathbf{y}(t-\Delta t+(k-m)h)\right)\right] \\
&= \sum_{l=1-q}^{-1} \left(\sum_{k=0}^{q-1+l} \left(\sum_{m=1}^{H} \lambda_1^{m-1} \left(\mathbf{c}_{p,n,w}\right)_{k+1} \left(\sum_{\substack{m'=1 \\ m'=m-l}}^{H} \lambda_2^{m'-1} \left(\mathbf{c}_{p,n,w}\right)_{k-l+1}\right) \operatorname{Var}\left[\mathbf{d}_\mathbf{y}(t-\Delta t+(k-m)h)\right]\right)\right) \\
&\quad + \sum_{l=1}^{q-1} \left(\sum_{k=l}^{q-1} \left(\sum_{m=1}^{H} \lambda_1^{m-1} \left(\mathbf{c}_{p,n,w}\right)_{k+1} \left(\sum_{\substack{m'=1 \\ m'=m-l}}^{H} \lambda_2^{m'-1} \left(\mathbf{c}_{p,n,w}\right)_{k-l+1}\right) \operatorname{Var}\left[\mathbf{d}_\mathbf{y}(t-\Delta t+(k-m)h)\right]\right)\right) \\
&\quad + \sum_{k=0}^{q-1} \left(\sum_{m=1}^{H} \lambda_1^{m-1} \left(\mathbf{c}_{p,n,w}\right)_{k+1} \left(\sum_{\substack{m'=1 \\ m'=m}}^{H} \lambda_2^{m'-1} \left(\mathbf{c}_{p,n,w}\right)_{k+1}\right) \operatorname{Var}\left[\mathbf{d}_\mathbf{y}(t-\Delta t+(k-m)h)\right]\right) \\
&= \operatorname{Var}\left[\mathbf{d}_\mathbf{y}(t)\right] \sum_{l=1}^{\min(H,q-1)} \frac{\lambda_2^l \left(1-(\lambda_1\lambda_2)^{H-l}\right)}{1-\lambda_1\lambda_2} \sum_{k=l}^{q-1} \left(\mathbf{c}_{p,n,w}\right)_{k+1} \left(\mathbf{c}_{p,n,w}\right)_{k-l+1} \\
&\quad + \operatorname{Var}\left[\mathbf{d}_\mathbf{y}(t)\right] \sum_{l=1}^{\min(H,q-1)} \frac{\lambda_1^l \left(1-(\lambda_1\lambda_2)^{H-l}\right)}{1-\lambda_1\lambda_2} \sum_{k=l}^{q-1} \left(\mathbf{c}_{p,n,w}\right)_{k+1} \left(\mathbf{c}_{p,n,w}\right)_{k-l+1} \\
&\quad + \operatorname{Var}\left[\mathbf{d}_\mathbf{y}(t)\right] \frac{1-(\lambda_1\lambda_2)^H}{1-\lambda_1\lambda_2} \sum_{k=0}^{q-1} \left(\mathbf{c}_{p,n,w}\right)_{k+1}^2 \\
&= \operatorname{Var}\left[\mathbf{d}_\mathbf{y}(t)\right] \frac{\beta'_{p,n,q,w}(\lambda_1,\lambda_2,H)}{1-\lambda_1\lambda_2}
\end{aligned}
\tag{D.18}
$$

and in the covariance of $\sum_{m=1}^{H}\lambda_1^{m-1}h\mathbf{d}_{\mathbf{x}}(t-mh)$ and $\sum_{m=1}^{H}\lambda_2^{m-1}\frac{h^p}{p!}\mathscr{S}_{p,n,q,w}(\mathbf{d}_{\mathbf{y}},t-mh)$

$$
\begin{aligned}
&\operatorname{Cov}\left[\sum_{m=1}^{H}\lambda_1^{m-1}h\mathbf{d}_{\mathbf{x}}(t-mh),\sum_{m=1}^{H}\lambda_2^{m-1}\frac{h^p}{p!}\mathscr{S}_{p,n,q,w}(\mathbf{d}_{\mathbf{y}},t-mh)\right]\\
&=h\operatorname{Cov}\left[\textstyle\sum_{m=1}^{H}\lambda_1^{m-1}\mathbf{d}_{\mathbf{x}}(t-mh),\sum_{m'=1}^{H}\lambda_2^{m'-1}\left(\sum_{k=0}^{q-1}\left(\mathbf{c}_{p,n,w}\right)_{k+1}\mathbf{d}_{\mathbf{y}}(t+(-m'+k-q+1)h)\right)\right]\\
&=h\left(\textstyle\sum_{m=1}^{H}\lambda_1^{m-1}\left(\sum_{k=0}^{q-1}\left(\sum_{\substack{m'=1\\ m'=m+k-q+1}}^{H}\lambda_2^{m'-1}\left(\mathbf{c}_{p,n,w}\right)_{k+1}\right)\right)\operatorname{Cov}\left[\mathbf{d}_{\mathbf{x}}(t-mh),\mathbf{d}_{\mathbf{y}}(t-mh)\right]\right)\\
&=\operatorname{Cov}\left[\mathbf{d}_{\mathbf{x}}(t),\mathbf{d}_{\mathbf{y}}(t)\right]\sum_{k=\max(q-1-H,0)}^{q-1}\frac{h\lambda_1^{-(k-q+1)}\left(1-(\lambda_1\lambda_2)^{H+k-q+1}\right)}{1-\lambda_1\lambda_2}\left(\mathbf{c}_{p,n,w}\right)_{k+1}\\
&=\operatorname{Cov}\left[\mathbf{d}_{\mathbf{x}}(t),\mathbf{d}_{\mathbf{y}}(t)\right]\frac{h\gamma'_{p,n,q,w}(\lambda_1,\lambda_2,H)}{1-\lambda_1\lambda_2}.
\end{aligned}
\tag{D.19}
$$

□

D.2 Proof of Proposition 5.1

Since $\mathscr{D}_q(\tilde{\mathbf{y}},t)=\mathscr{S}_{1,1,q,q-1}(\tilde{\mathbf{y}},t)$, the following equations are a consequence of Appendix D.1:

$$
\mathbf{G}_1=\begin{bmatrix}q & 0\\ 0 & \frac{q(q^2-1)}{12}\end{bmatrix},
\tag{D.20}
$$

$$
\mathbf{A}_1=\mathbf{G}_1^{-1}=\begin{bmatrix}\frac{1}{q} & 0\\ 0 & \frac{12}{q(q^2-1)}\end{bmatrix},
\tag{D.21}
$$

$$
\left(\mathbf{C}_1\right)_{k+1,m+1}=\sum_{i=0}^{1}\left(k-\tfrac{q-1}{2}\right)^i\left(\mathbf{A}_1\right)_{i+1,m+1},\qquad k=0,\dots,q-1,\qquad m=0,1,
\tag{D.22}
$$

$$
\begin{aligned}
c_{k+1} &= \left(\mathbf{c}_{1,1,q-1}\right)_{k+1} \\
&= \sum_{m=1}^{1} m \left(\tfrac{q-1}{2}\right)^{m-1} \left(\mathbf{C}_1\right)_{k+1,m+1} \\
&= \left(\mathbf{C}_1\right)_{k+1,2} \\
&= \sum_{i=0}^{1} \left(k - \tfrac{q-1}{2}\right)^{i} \left(\mathbf{A}_1\right)_{i+1,2} \\
&= \frac{12\left(k - \frac{q-1}{2}\right)}{q\left(q^2-1\right)}, \qquad k = 0, \ldots, q-1.
\end{aligned} \tag{D.23}
$$

These results have the following consequences:

$$
\sum_{k=0}^{q-1} c_{k+1}^2 = \frac{12}{q\left(q^2-1\right)}, \tag{D.24}
$$

$$
\sum_{k=l}^{q-1} c_{k+1} c_{k-l+1} = \frac{12\left(q-l\right)}{q^2\left(q^2-1\right)} - \frac{24\left(q^2-l^2\right)l}{\left(q\left(q^2-1\right)\right)^2}, \qquad l = 0, \ldots, q-1. \tag{D.25}
$$

It can also be proven that

$$
\sum_{k=0}^{q-2} b_{k+1} = 1. \tag{D.26}
$$

From the proposition in Appendix D.1 and the fact that the measurements $\tilde{\mathbf{y}}(t)$ are corrupted by zero-mean noise, it is possible to find the expected value of $\mathscr{D}_q(\tilde{\mathbf{y}}, t)$ and $\mathscr{R}_q(\dot{\mathbf{y}}, t)$

since

$$\begin{aligned}
\mathrm{E}\left[\mathscr{D}_q(\tilde{\mathbf{y}},t)\right] &= \mathscr{D}_q(\mathbf{y},t) \\
&= \sum_{k=0}^{q-1} c_{k+1} \int_{q-1}^{k} \dot{\mathbf{y}}(t-\Delta t+\xi h)\mathrm{d}\xi \\
&= -\sum_{k=0}^{q-1} c_{k+1} \int_{k}^{q-1} \dot{\mathbf{y}}(t-\Delta t+\xi h)\mathrm{d}\xi \\
&= -\sum_{k=0}^{q-1} c_{k+1} \left(\sum_{k'=k}^{q-2} \int_{k'}^{k'+1} \dot{\mathbf{y}}(t-\Delta t+\xi h)\mathrm{d}\xi \right) \\
&= -\sum_{k'=0}^{q-2} \left(\sum_{k=0}^{k'} c_{k+1} \right) \int_{k'}^{k'+1} \dot{\mathbf{y}}(t-\Delta t+\xi h)\mathrm{d}\xi \\
&= \sum_{k'=0}^{q-2} \left(\sum_{k=0}^{k'} \frac{12\left(\frac{q-1}{2}-k\right)}{q\left(q^2-1\right)} \right) \int_{k'}^{k'+1} \dot{\mathbf{y}}(t-\Delta t+\xi h)\mathrm{d}\xi \\
&= \sum_{k'=0}^{q-2} \left(12\frac{\frac{(k'+1)(q-1)}{2} - \frac{(k'+1)k'}{2}}{q\left(q^2-1\right)} \right) \int_{k'}^{k'+1} \dot{\mathbf{y}}(t-\Delta t+\xi h)\mathrm{d}\xi \\
&= \sum_{k'=0}^{q-2} \left(\frac{6\left(q-1-k'\right)\left(k'+1\right)}{q\left(q^2-1\right)} \right) \int_{k'}^{k'+1} \dot{\mathbf{y}}(t-\Delta t+\xi h)\mathrm{d}\xi
\end{aligned} \tag{D.27}$$

and

$$b_{k+1} = \frac{6\left(q-1-k\right)\left(k+1\right)}{q\left(q^2-1\right)} > 0, \qquad k = 0,\ldots,q-2, \tag{D.28}$$

which implies that

$$\begin{aligned}
\mathrm{E}\left[\mathscr{D}_q(\tilde{\mathbf{y}},t)\right] &= \sum_{k=0}^{q-2} b_{k+1} \int_{k}^{k+1} \dot{\mathbf{y}}(t-\Delta t+\xi h)\mathrm{d}\xi \\
&= \dot{\mathbf{y}}(t) - \left(\sum_{k=0}^{q-2} b_{k+1} \int_{k}^{k+1} \left(\dot{\mathbf{y}}(t) - \dot{\mathbf{y}}(t-\Delta t+\xi h)\right) \mathrm{d}\xi \right) \\
&= \dot{\mathbf{y}}(t) - \mathscr{R}_q(\dot{\mathbf{y}},t),
\end{aligned} \tag{D.29}$$

and, from the fact that the measurements $\tilde{\mathbf{y}}(t-mh)$ and $\tilde{\mathbf{x}}(t-mh)$ at different time instants, for $m = 0,\ldots,H$, are independent and identically distributed, the covariance of

$\sum_{m=1}^{H} \lambda_1^{m-1} h \mathscr{D}_q(\mathbf{d}_\mathbf{y}, t-mh)$ and $\sum_{m=1}^{H} \lambda_2^{m-1} h \mathscr{D}_q(\mathbf{d}_\mathbf{y}, t-mh)$

$$
\begin{aligned}
&\operatorname{Cov}\left[\sum_{m=1}^{H} \lambda_1^{m-1} h \mathscr{D}_q(\mathbf{d}_\mathbf{y}, t-mh), \sum_{m=1}^{H} \lambda_2^{m-1} h \mathscr{D}_q(\mathbf{d}_\mathbf{y}, t-mh)\right] \\
&= \operatorname{Var}\left[\mathbf{d}_\mathbf{y}(t)\right] \sum_{l=1}^{\min(H,q-1)} \frac{\lambda_2^l \left(1-(\lambda_1\lambda_2)^{H-l}\right)}{1-\lambda_1\lambda_2} \left(\sum_{k=l}^{q-1} c_{k+1} c_{k-l+1}\right) \\
&\quad + \operatorname{Var}\left[\mathbf{d}_\mathbf{y}(t)\right] \sum_{l=1}^{\min(H,q-1)} \frac{\lambda_1^l \left(1-(\lambda_1\lambda_2)^{H-l}\right)}{1-\lambda_1\lambda_2} \left(\sum_{k=l}^{q-1} c_{k+1} c_{k-l+1}\right) \\
&\quad + \operatorname{Var}\left[\mathbf{d}_\mathbf{y}(t)\right] \frac{1-(\lambda_1\lambda_2)^{H}}{1-\lambda_1\lambda_2} \left(\sum_{k=0}^{q-1} c_{k+1}^2\right) \\
&= \operatorname{Var}\left[\mathbf{d}_\mathbf{y}(t)\right] \sum_{l=1}^{\min(H,q-1)} \frac{\left(\lambda_2^l + \lambda_1^l\right)\left(1-(\lambda_1\lambda_2)^{H-l}\right)}{1-\lambda_1\lambda_2} \left(\frac{12(q-l)}{q^2(q^2-1)} - \frac{24(q^2-l^2)l}{\left(q(q^2-1)\right)^2}\right) \\
&\quad + \operatorname{Var}\left[\mathbf{d}_\mathbf{y}(t)\right] \frac{1-(\lambda_1\lambda_2)^{H}}{1-\lambda_1\lambda_2} \frac{12}{q\left(q^2-1\right)} \\
&= \operatorname{Var}\left[\mathbf{d}_\mathbf{y}(t)\right] \frac{\beta_q(\lambda_1,\lambda_2,H)}{1-\lambda_1\lambda_2}
\end{aligned}
\tag{D.30}
$$

and the covariance of $\sum_{m=1}^{H} \lambda_1^{m-1} h \mathbf{d}_\mathbf{x}(t-mh)$ and $\sum_{m=1}^{H} \lambda_2^{m-1} h \mathscr{D}_q(\mathbf{d}_\mathbf{y}, t-mh)$

$$
\begin{aligned}
&\operatorname{Cov}\left[\sum_{m=1}^{H} \lambda_1^{m-1} h \mathbf{d}_\mathbf{x}(t-mh), \sum_{m=1}^{H} \lambda_2^{m-1} h \mathscr{D}_q(\mathbf{d}_\mathbf{y}, t-mh)\right] \\
&= \operatorname{Cov}\left[\mathbf{d}_\mathbf{x}(t), \mathbf{d}_\mathbf{y}(t)\right] \sum_{k=\max(q-1-H,0)}^{q-1} h \frac{\lambda_1^{-(k-q+1)} \left(1-(\lambda_1\lambda_2)^{H+k-q+1}\right)}{1-\lambda_1\lambda_2} c_{k+1} \\
&= \operatorname{Cov}\left[\mathbf{d}_\mathbf{x}(t), \mathbf{d}_\mathbf{y}(t)\right] \frac{h\gamma_q(\lambda_1,\lambda_2,H)}{1-\lambda_1\lambda_2}.
\end{aligned}
\tag{D.31}
$$

Note that, for any μ such that $0 < \mu < 1$,

$$
\lim_{h\to 0} q - 1 = 2\alpha \lim_{h\to 0} h^{-\mu} = \infty. \tag{D.32}
$$

This implies that

$$\begin{aligned}
&\lim_{h\to 0} \operatorname{Cov}\left[\sum_{m=1}^{H} \lambda_1^{m-1} h \mathscr{D}_q(\mathbf{d}_\mathbf{y}, t-mh), \sum_{m=1}^{H} \lambda_2^{m-1} h \mathscr{D}_q(\mathbf{d}_\mathbf{y}, t-mh)\right] \\
&= \operatorname{Var}\left[\mathbf{d}_\mathbf{y}(t)\right] \lim_{h\to 0} \frac{\beta_q(\lambda_1,\lambda_2,H)}{1-\lambda_1\lambda_2} \\
&= \mathbf{0}
\end{aligned} \tag{D.33}$$

and

$$\begin{aligned}
&\lim_{h\to 0} \operatorname{Cov}\left[\sum_{m=1}^{H} \lambda_1^{m-1} h \mathbf{d}_\mathbf{x}(t-mh), \sum_{m=1}^{H} \lambda_2^{m-1} h \mathscr{D}_q(\mathbf{d}_\mathbf{y}, t-mh)\right] \\
&= \operatorname{Cov}\left[\mathbf{d}_\mathbf{x}(t), \mathbf{d}_\mathbf{y}(t)\right] \lim_{h\to 0} \frac{h\gamma_q(\lambda_1,\lambda_2,H)}{1-\lambda_1\lambda_2} \\
&= \operatorname{Cov}\left[\mathbf{d}_\mathbf{x}(t), \mathbf{d}_\mathbf{y}(t)\right] \lim_{h\to 0} \frac{\tau\left(1-\sqrt{\lambda_1\lambda_2}\right)\gamma_q(\lambda_1,\lambda_2,H)}{1-\lambda_1\lambda_2} \\
&= \mathbf{0}.
\end{aligned} \tag{D.34}$$

D.3 Bias and Variance of the Rate Estimator

Lemma D.2. *Consider the rate estimator $\hat{\mathbf{r}}_u(t)$ given in Eq.* (5.26) *and let Assumptions 5.2–5.5 hold. Then, the bias, variance and autocorrelations of the estimator $\hat{\mathbf{r}}_u(t)$ are:*

$$\mathrm{E}\left[\hat{\mathbf{r}}_u(t)\right] - \mathbf{r}_u(t) = \sum_{k=0}^{q-2} b_{k+1} \int_k^{k+1} \left(\mathbf{r}_u(t-\Delta t+\xi h) - \mathbf{r}_u(t)\right) \mathrm{d}\xi, \tag{D.35}$$

$$\operatorname{Var}\left[\hat{\mathbf{r}}_u(t)\right] = \left(\sum_{k=0}^{q-1} c_{k+1}^2\right) \frac{\operatorname{Var}\left[\tilde{\mathbf{y}}_r(t)\right]}{h^2}, \tag{D.36}$$

$$\operatorname{Cov}\left[\hat{\mathbf{r}}_u(t), \hat{\mathbf{r}}_u(t-lh)\right] = \left(\sum_{k=l}^{q-1} c_{k+1} c_{k-l+1}\right) \frac{\operatorname{Var}\left[\tilde{\mathbf{y}}_r(t)\right]}{h^2}, \qquad \forall l = 0,\dots,q-1, \tag{D.37}$$

if and only if

$$\begin{cases} c_1 + b_1 = 0 \\ c_{k+1} + b_{k+1} - b_k = 0, \quad \forall k = 1,\dots,q-1 \\ b_q = 0 \\ \sum_{k=0}^{q-2} b_{k+1} - 1 = 0 \end{cases}. \tag{D.38}$$

Proof. Since the functions $\mathbf{y}_r$ are Lipschitz continuous (due to the fact that $\mathbf{y}_r$ is described

by a differential equation, with $\dot{\mathbf{y}}_r$ bounded), it can be shown that, for all $k = 0, \ldots, q-2$,

$$h \int_k^{k+1} \dot{\mathbf{y}}_r(t - \Delta t + \xi h) \mathrm{d}\xi = \mathbf{y}_r(t - \Delta t + (k+1)h) - \mathbf{y}_r(t - \Delta t + kh), \tag{D.39}$$

which, along with Eq. (5.26) and Assumption 5.3, implies that the expected value of the estimator $\hat{\mathbf{r}}_u(t)$ is:

$$\begin{aligned}
\mathrm{E}\left[\hat{\mathbf{r}}_u(t)\right] &= \sum_{k=0}^{q-1} \frac{c_{k+1}}{h} \mathbf{y}_r(t - \Delta t + kh) - \left(\sum_{k=0}^{q-1} b_{k+1} \mathscr{T} \mathbf{s}_a(t - \Delta t + kh) \right) \\
&= \sum_{k=0}^{q-2} \frac{b_{k+1}}{h} \left(\mathbf{y}_r(t - \Delta t + kh) - \mathbf{y}_r(t - \Delta t + (k+1)h) \right) \\
&\quad + \sum_{k=0}^{q-1} \frac{c_{k+1}}{h} \mathbf{y}_r(t - \Delta t + kh) \\
&\quad + \sum_{k=0}^{q-2} b_{k+1} \int_k^{k+1} \dot{\mathbf{y}}_r(t - \Delta t + \xi h) \mathrm{d}\xi - \left(\sum_{k=0}^{q-1} b_{k+1} \mathscr{T} \mathbf{s}_a(t - \Delta t + kh) \right) \\
&= \frac{c_1 + b_1}{h} \mathbf{y}_r(t - \Delta t) + \sum_{k=1}^{q-1} \frac{c_{k+1} + b_{k+1} - b_k}{h} \mathbf{y}_r(t - \Delta t + kh) \\
&\quad - \frac{b_q}{h} \mathbf{y}_r(t) - b_q \mathscr{T} \mathbf{s}_a(t) \\
&\quad + \sum_{k=0}^{q-2} b_{k+1} \int_k^{k+1} \dot{\mathbf{y}}_r(t - \Delta t + \xi h) \mathrm{d}\xi - \left(\sum_{k=0}^{q-2} b_{k+1} \mathscr{T} \mathbf{s}_a(t - \Delta t + kh) \right).
\end{aligned} \tag{D.40}$$

Then, it follows from Assumption 5.2 that the bias of the estimator $\hat{\mathbf{r}}_u(t)$ is

$$\begin{aligned}
\mathrm{E}\left[\hat{\mathbf{r}}_u(t)\right] - \mathbf{r}_u(t) = &\underbrace{\frac{c_1 + b_1}{h}}_{0}\mathbf{y}_r(t-\Delta t) + \sum_{k=1}^{q-1}\underbrace{\frac{c_{k+1} + b_{k+1} - b_k}{h}}_{0}\mathbf{y}_r(t-\Delta t+kh) \\
&- \underbrace{\frac{b_q}{h}}_{0}\mathbf{y}_r(t) - \underbrace{b_q}_{0}\mathscr{T}\mathbf{s}_a(t) \\
&+ \sum_{k=0}^{q-2} b_{k+1}\int_k^{k+1}\mathbf{r}_u(t-\Delta t+\xi h)\mathrm{d}\xi - \underbrace{\left(\sum_{k=0}^{q-2} b_{k+1}\right)}_{1}\mathbf{r}_u(t) \\
&+ \sum_{k=0}^{q-2} b_{k+1}\mathscr{T}\underbrace{\left(\int_k^{k+1}\mathbf{s}_a(t-\Delta t+\xi h)\mathrm{d}\xi - \mathbf{s}_a(t-\Delta t+kh)\right)}_{\mathbf{0}} \\
= &\sum_{k=0}^{q-2} b_{k+1}\int_k^{k+1}\left(\mathbf{r}_u(t-\Delta t+\xi h) - \mathbf{r}_u(t)\right)\mathrm{d}\xi
\end{aligned} \tag{D.41}$$

if and only if the following conditions hold:

$$\begin{cases} c_1 + b_1 = 0 \\ c_{k+1} + b_{k+1} - b_k = 0, \quad \forall k = 1,\ldots,q-1 \\ b_q = 0 \\ \sum_{k=0}^{q-2} b_{k+1} - 1 = 0 \end{cases}. \tag{D.42}$$

Taking into account the general form of the estimator $\hat{\mathbf{r}}_u(t)$ in Eq. (5.26) and Assumptions 5.4–5.5, the variance and the autocorrelations of this estimator are given by:

$$\begin{aligned}
\mathrm{Var}\left[\hat{\mathbf{r}}_u(t)\right] &= \mathrm{Var}\left[\sum_{k=0}^{q-1}\frac{c_{k+1}}{h}\tilde{\mathbf{y}}_r(t-\Delta t+kh) - \left(\sum_{k=0}^{q-1} b_{k+1}\mathscr{T}\tilde{\mathbf{s}}_a(t-\Delta t+kh)\right)\right] \\
&= \mathrm{Var}\left[\sum_{k=0}^{q-1}\frac{c_{k+1}}{h}\tilde{\mathbf{y}}_r(t-\Delta t+kh)\right] \\
&= \sum_{k=0}^{q-1}\frac{c_{k+1}^2}{h^2}\mathrm{Var}\left[\tilde{\mathbf{y}}_r(t-\Delta t+kh)\right] \\
&= \left(\sum_{k=0}^{q-1} c_{k+1}^2\right)\frac{\mathrm{Var}\left[\tilde{\mathbf{y}}_r(t)\right]}{h^2},
\end{aligned} \tag{D.43}$$

$$
\begin{aligned}
&\operatorname{Cov}\left[\hat{\mathbf{r}}_u(t), \hat{\mathbf{r}}_u(t-lh)\right] \\
&= \operatorname{Cov}\left[\sum_{k=0}^{q-1} \frac{c_{k+1}}{h}\tilde{\mathbf{y}}_r(t-\Delta t+kh), \sum_{k=0}^{q-1} \frac{c_{k+1}}{h}\tilde{\mathbf{y}}_r(t-\Delta t+kh-lh)\right] \\
&= \sum_{k=l}^{q-1} \frac{c_{k+1}c_{k-l+1}}{h^2}\operatorname{Var}\left[\tilde{\mathbf{y}}_r(t-\Delta t+kh-lh)\right] \\
&= \left(\sum_{k=l}^{q-1} c_{k+1}c_{k-l+1}\right)\frac{\operatorname{Var}\left[\tilde{\mathbf{y}}_r(t)\right]}{h^2}, \qquad \forall l = 0,\ldots,q-1.
\end{aligned} \tag{D.44}
$$

□

D.4 Proof of Proposition 5.2

The convolution coefficients $c_1,\ldots,c_q,b_1,\ldots,b_q$ of the *optimal estimator* $\hat{\mathbf{r}}_u(t)$ minimize the variance of the estimator, $\operatorname{Var}\left[\hat{\mathbf{r}}_u(t)\right]$, while also ensuring that it is unbiased, that is, its expected value $\operatorname{E}\left[\hat{\mathbf{r}}_u(t)\right]$ is equal to $\mathbf{r}_u(t)$. These conditions imply that these coefficients are given by the solution to the following optimization problem, for any nonzero n_r-dimensional vector $\mathbf{a}$:

$$
\min_{c_1,\ldots,c_q,b_1,\ldots,b_q} \quad \mathbf{a}^{\mathrm{T}}\operatorname{Var}\left[\hat{\mathbf{r}}_u(t)\right]\mathbf{a} \tag{D.45a}
$$

$$
\text{s.t.} \quad \operatorname{E}\left[\hat{\mathbf{r}}_u(t)\right] - \mathbf{r}_u(t) = \mathbf{0}. \tag{D.45b}
$$

The cost function to minimize is given by Eq. (D.36) in Lemma D.2. Furthermore, Assumption 5.1 implies that the bias in Eq. (D.35) equals zero if and only if the constraints in Eq. (D.38) are satisfied. Hence, the optimal convolution coefficients $c_1^*,\ldots,c_q^*,b_1^*,\ldots,b_q^*$ correspond to the solution to the following optimization problem:

$$
\min_{c_1,\ldots,c_q,b_1,\ldots,b_q} \quad \left(\sum_{k=0}^{q-1} c_{k+1}^2\right)\mathbf{a}^{\mathrm{T}}\frac{\operatorname{Var}\left[\tilde{\mathbf{y}}_r(t)\right]}{h^2}\mathbf{a} \tag{D.46a}
$$

$$
\text{s.t.} \quad c_1 + b_1 = 0, \tag{D.46b}
$$

$$
c_{k+1} + b_{k+1} - b_k = 0, \quad \forall k = 1,\ldots,q-1, \tag{D.46c}
$$

$$
b_q = 0, \tag{D.46d}
$$

$$
\sum_{k=0}^{q-2} b_{k+1} - 1 = 0. \tag{D.46e}
$$

This optimization problem is equivalent to

$$\min_{b_1,\dots,b_{q-1}} \quad (-b_1)^2 + \sum_{k=1}^{q-2} (b_k - b_{k+1})^2 + b_{q-1}^2 \tag{D.47a}$$

$$\text{s.t.} \quad \sum_{k=0}^{q-2} b_{k+1} - 1 = 0, \tag{D.47b}$$

for which the Lagrangian function is:

$$\mathscr{L}(b_1,\dots,b_{q-1},\lambda) = (-b_1)^2 + \sum_{k=1}^{q-2} (b_k - b_{k+1})^2 + b_{q-1}^2 + \lambda \left(\sum_{k=0}^{q-2} b_{k+1} - 1 \right). \tag{D.48}$$

Since the optimization problem (D.47) is convex, the global solution is obtained by solving the following system of equations:

$$\begin{cases} 0 = \frac{\partial \mathscr{L}}{\partial b_1}(b_1^*,\dots,b_{q-1}^*,\lambda^*) = 2b_1^* + 2\left(b_1^* - b_2^*\right) + \lambda^* \\ 0 = \frac{\partial \mathscr{L}}{\partial b_2}(b_1^*,\dots,b_{q-1}^*,\lambda^*) = 2\left(b_2^* - b_1^*\right) + 2\left(b_2^* - b_3^*\right) + \lambda^* \\ \vdots \\ 0 = \frac{\partial \mathscr{L}}{\partial b_{q-1}}(b_1^*,\dots,b_{q-1}^*,\lambda^*) = 2\left(b_{q-1}^* - b_{q-2}^*\right) + 2b_{q-1}^* + \lambda^* \\ 0 = \frac{\partial \mathscr{L}}{\partial \lambda}(b_1^*,\dots,b_{q-1}^*,\lambda^*) = \sum_{k=0}^{q-2} b_{k+1}^* - 1 \end{cases}, \tag{D.49}$$

which gives

$$\begin{cases} b_{k+1}^* = \frac{6(q-k-1)(k+1)}{q(q^2-1)}, \quad \forall k = 0,\dots,q-1 \\ \lambda^* = -\frac{24}{q(q^2-1)} \end{cases}, \tag{D.50}$$

and implies:

$$c_{k+1}^* = \frac{12\left(k - \frac{q-1}{2}\right)}{q\left(q^2-1\right)}, \quad \forall k = 0,\dots,q-1. \tag{D.51}$$

The corresponding value of the variance is:

$$\text{Var}\left[\hat{\mathbf{r}}_u(t)\right] = \left(\sum_{k=0}^{q-1} {c_{k+1}^*}^2 \right) \frac{\text{Var}\left[\tilde{\mathbf{y}}_r(t)\right]}{h^2} = \frac{12}{q\left(q^2-1\right)} \frac{\text{Var}\left[\tilde{\mathbf{y}}_r(t)\right]}{h^2}. \tag{D.52}$$

E Appendix of Chapter 6

E.1 Proof of Proposition 6.1

We would like to prove that, under the conditions in Proposition 6.1, the following equations hold:

$$\begin{aligned}
\mathbf{u}(t+h) = &\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)(\mathbf{v}(t)-\mathbf{w}(t)) \\
&+ \left(\exp\left(-\mathbf{T}_a^{-1}h\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}\right)\mathbf{u}(t) \\
&+ \left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u,t) \\
&- \left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_\mathbf{y},t) \\
&- \left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t),
\end{aligned} \tag{E.1}$$

$$\begin{aligned}
\mathbf{x}(t+h) = &\mathbf{x}(t) + h\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{v}(t) \\
&- \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\mathbf{v}(t) \\
&+ \mathbf{F}\int_0^h (h-\zeta)\,\dot{\mathbf{r}}_u(t+\zeta)\mathrm{d}\zeta + h\mathbf{d}_{\mathbf{U}_a}(t)\mathbf{w}(t) \\
&+ \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}h\right)\mathbf{u}(t) \\
&+ \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\mathbf{w}(t) \\
&+ h\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u,t) \\
&- \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u,t) \\
&- h\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_\mathbf{y},t) \\
&+ \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_\mathbf{y},t) \\
&- h\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t) \\
&+ \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t).
\end{aligned} \tag{E.2}$$

First, let us note that

$$
\begin{aligned}
&\tilde{\mathbf{U}}_a(t)\left(\mathbf{v}(t)-\tilde{\boldsymbol{\beta}}_a(t)-\mathbf{F}\hat{\mathbf{r}}_u(t)\right)\\
&=\left(\mathbf{I}_{n_x}-\mathbf{D}\right)\tilde{\tilde{\mathbf{u}}}(t)\\
&\quad+\mathbf{D}h^{-1}\int_0^h\left(\mathbf{u}(t+\zeta)+\mathbf{d}_{\bar{\mathbf{u}}}(t)+\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\left(\mathbf{d}_{\mathbf{u}}(t)-\mathbf{d}_{\bar{\mathbf{u}}}(t)\right)\right)\mathrm{d}\zeta\\
&=\left(\mathbf{I}_{n_x}-\mathbf{D}\right)\tilde{\tilde{\mathbf{u}}}(t)\\
&\quad+\mathbf{D}h^{-1}\int_0^h\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\left(\mathbf{u}(t)+\mathbf{d}_{\mathbf{u}}(t)\right)\mathrm{d}\zeta\\
&\quad+\mathbf{D}h^{-1}\int_0^h\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\bar{\mathbf{u}}(t)+\mathbf{d}_{\bar{\mathbf{u}}}(t)\right)\mathrm{d}\zeta\\
&=\left(\mathbf{I}_{n_x}-\mathbf{D}\right)\tilde{\tilde{\mathbf{u}}}(t)\\
&\quad+\mathbf{D}\mathbf{T}_a h^{-1}\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}h\right)\right)\tilde{\mathbf{u}}(t)\\
&\quad+\mathbf{D}\left(\mathbf{I}_{n_x}-\mathbf{T}_a h^{-1}\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}h\right)\right)\right)\tilde{\tilde{\mathbf{u}}}(t)
\end{aligned}
\tag{E.3}
$$

implies that

$$
\tilde{\tilde{\mathbf{u}}}(t)=\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\left(\mathbf{v}(t)-\tilde{\boldsymbol{\beta}}_a(t)-\mathbf{F}\hat{\mathbf{r}}_u(t)\right)-\mathbf{W}\tilde{\mathbf{u}}(t),
\tag{E.4}
$$

which results in

$$
\begin{aligned}
\mathbf{u}(t+\zeta)&=\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\bar{\mathbf{u}}(t)+\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\mathbf{u}(t)\\
&=\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\left(\mathbf{v}(t)-\tilde{\boldsymbol{\beta}}_a(t)-\mathbf{F}\hat{\mathbf{r}}_u(t)\right)\\
&\quad-\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\mathbf{W}\tilde{\mathbf{u}}(t)\\
&\quad-\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\mathbf{d}_{\bar{\mathbf{u}}}(t)+\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\mathbf{u}(t)\\
&=\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\left(\mathbf{v}(t)-\mathbf{w}(t)\right)\\
&\quad+\left(\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}\right)\mathbf{u}(t)\\
&\quad-\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\left(\hat{\mathbf{r}}_u(t)-\mathbf{r}_u(t)\right)\\
&\quad-\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{d}_{\bar{\mathbf{u}}}(t)+\mathbf{W}\mathbf{d}_{\mathbf{u}}(t)\right)\\
&\quad-\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{d}_{\boldsymbol{\beta}_a}(t)\\
&=\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\left(\mathbf{v}(t)-\mathbf{w}(t)\right)\\
&\quad+\left(\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}\right)\mathbf{u}(t)\\
&\quad+\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u,t)\\
&\quad-\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_{\mathbf{y}},t)\\
&\quad-\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t)
\end{aligned}
\tag{E.5}
$$

and

$$\begin{aligned}\mathbf{u}(t+h) = &\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)(\mathbf{v}(t)-\mathbf{w}(t))\\ &+\left(\exp\left(-\mathbf{T}_a^{-1}h\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}\right)\mathbf{u}(t)\\ &+\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u,t)\\ &-\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_\mathbf{y},t)\\ &-\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t).\end{aligned} \tag{E.6}$$

The proposition can be completely proven by replacing $\mathbf{u}(t+\zeta)$ in Eq. (6.42), which yields

$$\begin{aligned}\dot{\mathbf{x}}(t+\zeta) = &\mathbf{F}\mathbf{r}_u(t+\zeta)+\boldsymbol{\beta}_a(t)\\ &+\mathbf{B}_a(t)\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)(\mathbf{v}(t)-\mathbf{w}(t))\\ &+\mathbf{B}_a(t)\left(\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}\right)\mathbf{u}(t)\\ &+\mathbf{B}_a(t)\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u,t)\\ &-\mathbf{B}_a(t)\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_\mathbf{y},t)\\ &-\mathbf{B}_a(t)\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t)\\ = &\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{v}(t)\\ &-\mathbf{B}_a(t)\left(\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{v}(t)\\ &+\mathbf{F}\int_0^\zeta \dot{\mathbf{r}}_u(t+\tau)\mathrm{d}\tau+\mathbf{d}_{\mathbf{U}_a}(t)\left(\mathbf{F}\mathbf{r}_u(t)+\boldsymbol{\beta}_a(t)\right)\\ &+\mathbf{B}_a(t)\left(\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}\right)\mathbf{u}(t)\\ &+\mathbf{B}_a(t)\left(\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{w}(t)\\ &+\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u,t)\\ &-\mathbf{B}_a(t)\left(\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u,t)\\ &-\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_\mathbf{y},t)\\ &+\mathbf{B}_a(t)\left(\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_\mathbf{y},t)\\ &-\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t)\\ &+\mathbf{B}_a(t)\left(\exp\left(-\mathbf{T}_a^{-1}\zeta\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}\right)\tilde{\mathbf{U}}_a(t)\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t),\end{aligned} \tag{E.7}$$

$$
\begin{aligned}
\mathbf{x}(t+\zeta) &= \mathbf{x}(t) + \int_0^{\zeta} \dot{\mathbf{x}}(t+\tau)\mathrm{d}\tau \\
&= \mathbf{x}(t) + \int_0^{\zeta} \left(\dot{\mathbf{x}}(t+\tau) - \mathbf{F}\dot{\mathbf{r}}_u(t+\tau)\right)\mathrm{d}\tau + \zeta\mathbf{F}\dot{\mathbf{r}}_u(t) \\
&\quad + \mathbf{F}\int_0^{\zeta} (\zeta-\tau)\,\ddot{\mathbf{r}}_u(t+\tau)\mathrm{d}\tau \\
&= \mathbf{x}(t) + \int_0^{\zeta} \left(\dot{\mathbf{x}}(t+\tau) - \mathbf{F}\int_0^{\tau} \ddot{\mathbf{r}}_u(t+\tau')\mathrm{d}\tau'\right)\mathrm{d}\tau \\
&\quad + \mathbf{F}\int_0^{\zeta} (\zeta-\tau)\,\ddot{\mathbf{r}}_u(t+\tau)\mathrm{d}\tau \\
&= \mathbf{x}(t) + \zeta\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{v}(t) \\
&\quad - \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right) - \mathbf{W}\zeta\right)\tilde{\mathbf{U}}_a(t)\mathbf{v}(t) \\
&\quad + \mathbf{F}\int_0^{\zeta} (\zeta-\tau)\,\ddot{\mathbf{r}}_u(t+\tau)\mathrm{d}\tau + \zeta\mathbf{d}_{\mathbf{U}_a}(t)\mathbf{w}(t) \\
&\quad + \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right) - \mathbf{W}\zeta\right)\mathbf{u}(t) \\
&\quad + \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right) - \mathbf{W}\zeta\right)\tilde{\mathbf{U}}_a(t)\mathbf{w}(t) \\
&\quad + \zeta\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u, t) \\
&\quad - \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right) - \mathbf{W}\zeta\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u, t) \\
&\quad - \zeta\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_{\mathbf{y}}, t) \\
&\quad + \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right) - \mathbf{W}\zeta\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_{\mathbf{y}}, t) \\
&\quad - \zeta\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t) \\
&\quad + \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}\zeta\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right) - \mathbf{W}\zeta\right)\tilde{\mathbf{U}}_a(t)\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t), \qquad \text{(E.8)}
\end{aligned}
$$

and

$$\begin{aligned}\mathbf{x}(t+h) = \mathbf{x}(t) &+ h\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{v}(t)\\ &- \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right) - \mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\mathbf{v}(t)\\ &+ \mathbf{F}\int_0^h (h-\zeta)\,\dot{\mathbf{r}}_u(t+\zeta)\mathrm{d}\zeta + h\mathbf{d}_{\mathbf{U}_a}(t)\mathbf{w}(t)\\ &+ \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right) - \mathbf{W}h\right)\mathbf{u}(t)\\ &+ \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right) - \mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\mathbf{w}(t)\\ &+ h\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u,t)\\ &- \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right) - \mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u,t)\\ &- h\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_\mathbf{y},t)\\ &+ \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right) - \mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_\mathbf{y},t)\\ &- h\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t)\\ &+ \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right) - \mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t). \end{aligned} \tag{E.9}$$

E.2 Proof of Proposition 6.2

First of all, let us prove that

$$\mathbf{v}(t) = \frac{\mathbf{x}^s(t+h) - \mathbf{x}^s(t)}{h} + \boldsymbol{\Gamma}\left(\mathbf{x}^s(t) - \tilde{\mathbf{x}}(t)\right) \tag{E.10}$$

implies that

$$\mathbf{v}(t) = \dot{\mathbf{x}}^s(t) + \frac{h}{2}\frac{\dot{\mathbf{x}}^s(t+h) - \dot{\mathbf{x}}^s(t)}{h} - \int_0^h \frac{2\zeta - h}{2h}\ddot{\mathbf{x}}^s(t+\zeta)\mathrm{d}\zeta + \boldsymbol{\Gamma}\left(\mathbf{x}^s(t) - \tilde{\mathbf{x}}(t)\right). \tag{E.11}$$

For that, one should note that

$$
\begin{aligned}
&\mathbf{x}^s(t+h)-\mathbf{x}^s(t)\\
&=\int_0^h \left(\dot{\mathbf{x}}^s(t+\zeta)-\dot{\mathbf{x}}^s(t+h)\right)\mathrm{d}\zeta + h\dot{\mathbf{x}}^s(t+h)\\
&=\int_0^h \left(\dot{\mathbf{x}}^s(t+\zeta)-\dot{\mathbf{x}}^s(t+h)\right)\mathrm{d}\zeta\\
&\quad + h\left(\dot{\mathbf{x}}^s(t)+\int_0^h \ddot{\mathbf{x}}^s(t+\zeta)\mathrm{d}\zeta + \tfrac{h}{2}\tfrac{\dot{\mathbf{x}}^s(t+h)-\dot{\mathbf{x}}^s(t)}{h} - \tfrac{1}{2}\int_0^h \ddot{\mathbf{x}}^s(t+\zeta)\mathrm{d}\zeta\right)\\
&=h\dot{\mathbf{x}}^s(t)+\tfrac{h^2}{2}\tfrac{\dot{\mathbf{x}}^s(t+h)-\dot{\mathbf{x}}^s(t)}{h}+\int_0^h \left(\dot{\mathbf{x}}^s(t+\zeta)-\dot{\mathbf{x}}^s(t+h)\right)\mathrm{d}\zeta + \tfrac{h}{2}\int_0^h \ddot{\mathbf{x}}^s(t+\zeta)\mathrm{d}\zeta\\
&=h\dot{\mathbf{x}}^s(t)+\tfrac{h^2}{2}\tfrac{\dot{\mathbf{x}}^s(t+h)-\dot{\mathbf{x}}^s(t)}{h}+\int_0^h \dot{\mathbf{x}}^s(t+\zeta)\mathrm{d}\zeta - \left[\zeta\dot{\mathbf{x}}^s(t+\zeta)\right]_0^h + \int_0^h \tfrac{h}{2}\ddot{\mathbf{x}}^s(t+\zeta)\mathrm{d}\zeta\\
&=h\dot{\mathbf{x}}^s(t)+\tfrac{h^2}{2}\tfrac{\dot{\mathbf{x}}^s(t+h)-\dot{\mathbf{x}}^s(t)}{h}-\int_0^h \zeta\ddot{\mathbf{x}}^s(t+\zeta)\mathrm{d}\zeta + \int_0^h \tfrac{h}{2}\ddot{\mathbf{x}}^s(t+\zeta)\mathrm{d}\zeta\\
&=h\dot{\mathbf{x}}^s(t)+\tfrac{h^2}{2}\tfrac{\dot{\mathbf{x}}^s(t+h)-\dot{\mathbf{x}}^s(t)}{h}-\int_0^h \left(\zeta-\tfrac{h}{2}\right)\ddot{\mathbf{x}}^s(t+\zeta)\mathrm{d}\zeta. \qquad \text{(E.12)}
\end{aligned}
$$

The control law in Eq. (6.57), along with Eqs. (E.1) and (E.2), implies that

$$
\begin{aligned}
\mathbf{x}(t+h) &= \mathbf{x}(t)+h\left(\frac{\mathbf{x}^s(t+h)-\mathbf{x}^s(t)}{h}+\boldsymbol{\Gamma}\left(\mathbf{x}^s(t)-\mathbf{x}(t)\right)\right)+\boldsymbol{\upsilon}_x(t)\\
&\quad -\mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\boldsymbol{\Gamma}\left(\mathbf{x}^s(t)-\mathbf{x}(t)\right)\\
&\quad -\mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\dot{\mathbf{x}}^s(t)\\
&\quad +\mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}h\right)\left(\mathbf{u}(t)+\tilde{\mathbf{U}}_a(t)\mathbf{w}(t)\right)\\
&=\mathbf{x}^s(t+h)+\boldsymbol{\upsilon}_x(t)\\
&\quad +\left(\mathbf{I}_{n_x}-h\boldsymbol{\Gamma}\right)\left(\mathbf{x}(t)-\mathbf{x}^s(t)\right)\\
&\quad +\mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\boldsymbol{\Gamma}\left(\mathbf{x}(t)-\mathbf{x}^s(t)\right)\\
&\quad -\mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\dot{\mathbf{x}}^s(t)\\
&\quad +\mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}h\right)\left(\mathbf{u}(t)+\tilde{\mathbf{U}}_a(t)\mathbf{w}(t)\right)\\
&=\mathbf{x}^s(t+h)+\boldsymbol{\upsilon}_x(t)\\
&\quad +\mathbf{M}_x\left(\mathbf{x}(t)-\mathbf{x}^s(t)\right)+\mathbf{M}_u\left(\mathbf{u}(t)+\tilde{\mathbf{U}}_a(t)\mathbf{w}(t)-\tilde{\mathbf{U}}_a(t)\dot{\mathbf{x}}^s(t)\right), \qquad \text{(E.13)}
\end{aligned}
$$

with

$$
\mathbf{M}_x=\mathbf{I}_{n_x}-h\boldsymbol{\Gamma}+\mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x}-\exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x}+\mathbf{W}\right)-\mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\boldsymbol{\Gamma}, \qquad \text{(E.14)}
$$

$$\mathbf{M}_u = \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x} + \mathbf{W}\right) - \mathbf{W}h\right), \tag{E.15}$$

$$\begin{aligned}
&\boldsymbol{\upsilon}_x(t)\\
&= h\mathbf{d}_{\mathbf{U}_a}(t)\boldsymbol{\Gamma}\left(\mathbf{x}(t) - \mathbf{x}^s(t)\right) + h\mathbf{d}_{\mathbf{U}_a}(t)\left(\mathbf{w}(t) - \dot{\mathbf{x}}^s(t)\right)\\
&\quad + \mathbf{F}\int_0^h \left(h-\zeta\right)\dot{\mathbf{r}}_u(t+\zeta)\mathrm{d}\zeta\\
&\quad - h\mathbf{d}_{\mathbf{U}_a}(t)\tfrac{h}{2}\tfrac{\dot{\mathbf{x}}^s(t+h)-\dot{\mathbf{x}}^s(t)}{h} + h\mathbf{d}_{\mathbf{U}_a}(t)\int_0^h \tfrac{2\zeta-h}{2h}\ddot{\mathbf{x}}^s(t+\zeta)\mathrm{d}\zeta\\
&\quad - \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x} + \mathbf{W}\right) - \mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\tfrac{h}{2}\tfrac{\dot{\mathbf{x}}^s(t+h)-\dot{\mathbf{x}}^s(t)}{h}\\
&\quad + \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x} + \mathbf{W}\right) - \mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\int_0^h \tfrac{2\zeta-h}{2h}\ddot{\mathbf{x}}^s(t+\zeta)\mathrm{d}\zeta\\
&\quad + h\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u, t)\\
&\quad - \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x} + \mathbf{W}\right) - \mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u, t)\\
&\quad - h\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_{\mathbf{y}}, t)\\
&\quad + \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x} + \mathbf{W}\right) - \mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_{\mathbf{y}}, t)\\
&\quad - h\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\left(\boldsymbol{\Gamma}\mathbf{d}_{\mathbf{x}}(t) + \mathbf{d}_{\bar{\boldsymbol{\beta}}_a}(t)\right)\\
&\quad + \mathbf{B}_a(t)\left(\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\left(\mathbf{I}_{n_x} + \mathbf{W}\right) - \mathbf{W}h\right)\tilde{\mathbf{U}}_a(t)\left(\boldsymbol{\Gamma}\mathbf{d}_{\mathbf{x}}(t) + \mathbf{d}_{\bar{\boldsymbol{\beta}}_a}(t)\right).
\end{aligned} \tag{E.16}$$

In particular, if

$$\mathbf{D} = \mathbf{I}_{n_x}, \tag{E.17}$$

then

$$\begin{aligned}
\mathbf{M}_u &= \mathbf{B}_a(t)\left(\mathbf{I}_{n_x} - \mathbf{D}\mathbf{T}_a h^{-1}\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\right)^{-1}\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\\
&\quad - \mathbf{B}_a(t)\left(\mathbf{I}_{n_x} - \mathbf{D}\mathbf{T}_a h^{-1}\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\right)^{-1}\mathbf{D}\mathbf{T}_a\left(\mathbf{I}_{n_x} - \exp\left(-\mathbf{T}_a^{-1}h\right)\right)\\
&= \mathbf{0}_{n_x\times n_x},
\end{aligned} \tag{E.18}$$

$$\begin{aligned}
\mathbf{M}_x &= \mathbf{I}_{n_x} - h\boldsymbol{\Gamma} + \mathbf{M}_u\tilde{\mathbf{U}}_a(t)\boldsymbol{\Gamma}\\
&= \mathbf{I}_{n_x} - h\boldsymbol{\Gamma},
\end{aligned} \tag{E.19}$$

$$
\begin{aligned}
\boldsymbol{\upsilon}_x(t) = & h\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\mathbf{F}\mathscr{R}_q(\mathbf{r}_u, t) + \mathbf{F}\int_0^h \left(h-\zeta\right)\dot{\mathbf{r}}_u(t+\zeta)\mathrm{d}\zeta \\
& + h\mathbf{d}_{\mathbf{U}_a}(t)\boldsymbol{\Gamma}\left(\mathbf{x}(t) - \mathbf{x}^s(t)\right) + h\mathbf{d}_{\mathbf{U}_a}(t)\left(\mathbf{w}(t) - \dot{\mathbf{x}}^s(t)\right) \\
& - h\mathbf{d}_{\mathbf{U}_a}(t)\tfrac{h}{2}\tfrac{\dot{\mathbf{x}}^s(t+h)-\dot{\mathbf{x}}^s(t)}{h} + h\mathbf{d}_{\mathbf{U}_a}(t)\int_0^h \tfrac{2\zeta-h}{2h}\ddot{\mathbf{x}}^s(t+\zeta)\mathrm{d}\zeta \\
& - h\left(\mathbf{I}_{n_x} - \mathbf{d}_{\mathbf{U}_a}(t)\right)\left(\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_{\mathbf{y}}, t) + \boldsymbol{\Gamma}\mathbf{d}_{\mathbf{x}}(t) + \mathbf{d}_{\bar{\boldsymbol{\beta}}_a}(t)\right),
\end{aligned} \tag{E.20}
$$

which can be represented as

$$
\begin{aligned}
\mathbf{x}(t) - \mathbf{x}^s(t) = & \left(\mathbf{I}_{n_x} - h\boldsymbol{\Gamma}\right)^n \left(\mathbf{x}(t-nh) - \mathbf{x}^s(t-nh)\right) \\
& + \sum_{m=1}^{n}\left(\mathbf{I}_{n_x} - h\boldsymbol{\Gamma}\right)^{m-1}\boldsymbol{\upsilon}_x(t-mh).
\end{aligned} \tag{E.21}
$$

Note that, since

$$
\begin{aligned}
\mathscr{R}_q(\mathbf{r}_u, t-mh) &= \sum_{k=0}^{q-2} b_{k+1}\int_k^{k+1}\left(\mathbf{r}_u(t-mh) - \mathbf{r}_u(t-mh-\Delta t+\xi h)\right)\mathrm{d}\xi \\
&= -\sum_{k=0}^{q-2} b_{k+1}\int_k^{k+1}(\xi-k)\left(-\dot{\mathbf{r}}_u(t-mh-\Delta t+\xi h)\right)h\mathrm{d}\xi \\
&\quad + \sum_{k=0}^{q-2} b_{k+1}\left[(\xi-k)\left(\mathbf{r}_u(t-mh) - \mathbf{r}_u(t-mh-\Delta t+\xi h)\right)\right]_k^{k+1} \\
&= h\sum_{k=0}^{q-2} b_{k+1}\int_k^{k+1}(\xi-k)\dot{\mathbf{r}}_u(t-mh-\Delta t+\xi h)\mathrm{d}\xi \\
&\quad + \sum_{k=0}^{q-2} b_{k+1}\left(\mathbf{r}_u(t-mh) - \mathbf{r}_u(t-mh-\Delta t+(k+1)h)\right) \\
&= h\sum_{k=0}^{q-2} b_{k+1}\int_k^{k+1}(\xi-k)\dot{\mathbf{r}}_u(t-mh-\Delta t+\xi h)\mathrm{d}\xi \\
&\quad + h\sum_{k=0}^{q-2} b_{k+1}\int_{k+1}^{q-1}\dot{\mathbf{r}}_u(t-mh-\Delta t+\xi h)\mathrm{d}\xi,
\end{aligned} \tag{E.22}
$$

the expected value of $\mathbf{x}(t)$ is given by

$$
\begin{aligned}
&\mathrm{E}\left[\mathbf{x}(t)\right] \\
&= \mathbf{x}^{s}(t) + \left(\mathbf{I}_{n_x} - h\boldsymbol{\Gamma}\right)^{n} \left(\mathbf{x}(t-nh) - \mathbf{x}^{s}(t-nh)\right) \\
&\quad + \sum_{m=1}^{n} \left(\mathbf{I}_{n_x} - h\boldsymbol{\Gamma}\right)^{m-1} h\mathbf{F}\mathscr{R}_q(\mathbf{r}_u, t-mh) \\
&\quad + \sum_{m=1}^{n} \left(\mathbf{I}_{n_x} - h\boldsymbol{\Gamma}\right)^{m-1} \mathbf{F} \int_0^h \left(h-\zeta\right) \dot{\mathbf{r}}_u(t-mh+\zeta)\mathrm{d}\zeta \\
&= \mathbf{x}^{s}(t) + \left(\mathbf{I}_{n_x} - h\boldsymbol{\Gamma}\right)^{n} \left(\mathbf{x}(t-nh) - \mathbf{x}^{s}(t-nh)\right) \\
&\quad + \sum_{m=1}^{n} \left(\mathbf{I}_{n_x} - h\boldsymbol{\Gamma}\right)^{m-1} h^2\mathbf{F} \left(\sum_{k=0}^{q-2} b_{k+1} \int_k^{k+1} \dot{\mathbf{r}}_u(t-mh-\Delta t+\xi h)(\xi-k)\,\mathrm{d}\xi \right) \\
&\quad + \sum_{m=1}^{n} \left(\mathbf{I}_{n_x} - h\boldsymbol{\Gamma}\right)^{m-1} h^2\mathbf{F} \left(\sum_{k=0}^{q-2} b_{k+1} \int_{k+1}^{q-1} \dot{\mathbf{r}}_u(t-mh-\Delta t+\xi h)\mathrm{d}\xi \right) \\
&\quad + \sum_{m=1}^{n} \left(\mathbf{I}_{n_x} - h\boldsymbol{\Gamma}\right)^{m-1} h^2\mathbf{F} \int_0^1 (1-\xi)\dot{\mathbf{r}}_u(t-mh+\xi h)\mathrm{d}\xi,
\end{aligned}
\tag{E.23}
$$

whereas the ith diagonal element of the covariance matrix of $\mathbf{x}(t)$ is given by

$$
\begin{aligned}
\sigma_{x_i}^2 &= \mathrm{Var}\left[x_i(t)\right] \\
&= \mathrm{Var}\left[\sum_{m=1}^{n}\left(1-h\boldsymbol{\Gamma}_{i,i}\right)^{m-1} h\left(\boldsymbol{\Gamma}\mathbf{d}_{\mathbf{x}}(t-mh)+\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t-mh)\right.\right. \\
&\quad \left.\left.+\ \mathbf{F}\boldsymbol{\mathscr{T}}\mathscr{D}_q(\mathbf{d}_{\mathbf{y}},t-mh)\right)_i\right] \\
&= \boldsymbol{\Gamma}_{i,i}\mathrm{Var}\left[\sum_{m=1}^{n}\left(1-h\boldsymbol{\Gamma}_{i,i}\right)^{m-1} h\left(d_{x_i}(t-mh)+\boldsymbol{\Gamma}_{i,i}^{-1}d_{\tilde{\beta}_{a,i}}(t-mh)\right)\right]\boldsymbol{\Gamma}_{i,i} \\
&\quad +(\mathbf{F}\boldsymbol{\mathscr{T}})_i\,\mathrm{Var}\left[\sum_{m=1}^{n}\left(1-h\boldsymbol{\Gamma}_{i,i}\right)^{m-1} h\mathscr{D}_q(\mathbf{d}_{\mathbf{y}},t-mh)\right](\mathbf{F}\boldsymbol{\mathscr{T}})_i^{\mathrm{T}} \\
&\quad +\boldsymbol{\Gamma}_{i,i}\mathrm{Cov}\left[\sum_{m=1}^{n}\left(1-h\boldsymbol{\Gamma}_{i,i}\right)^{m-1} h\left(d_{x_i}(t-mh)+\boldsymbol{\Gamma}_{i,i}^{-1}d_{\tilde{\beta}_{a,i}}(t-mh)\right),\right. \\
&\qquad \left.\sum_{m=1}^{n}\left(1-h\boldsymbol{\Gamma}_{i,i}\right)^{m-1} h\mathscr{D}_q(\mathbf{d}_{\mathbf{y}},t-mh)\right](\mathbf{F}\boldsymbol{\mathscr{T}})_i^{\mathrm{T}} \\
&\quad +(\mathbf{F}\boldsymbol{\mathscr{T}})_i\,\mathrm{Cov}\left[\sum_{m=1}^{n}\left(1-h\boldsymbol{\Gamma}_{i,i}\right)^{m-1} h\mathscr{D}_q(\mathbf{d}_{\mathbf{y}},t-mh),\right. \\
&\qquad \left.\sum_{m=1}^{n}\left(1-h\boldsymbol{\Gamma}_{i,i}\right)^{m-1} h\left(d_{x_i}(t-mh)+\boldsymbol{\Gamma}_{i,i}^{-1}d_{\tilde{\beta}_{a,i}}(t-mh)\right)\right]\boldsymbol{\Gamma}_{i,i} \\
&= \frac{h^2\boldsymbol{\Gamma}_{i,i}^2\left(1-\left(1-h\boldsymbol{\Gamma}_{i,i}\right)^{2n}\right)}{1-\left(1-h\boldsymbol{\Gamma}_{i,i}\right)^2}\mathrm{Var}\left[d_{x_i}(t)+\boldsymbol{\Gamma}_{i,i}^{-1}d_{\tilde{\beta}_{a,i}}(t)\right] \\
&\quad +\frac{\beta_q(1-h\boldsymbol{\Gamma}_{i,i},1-h\boldsymbol{\Gamma}_{i,i},n)}{1-\left(1-h\boldsymbol{\Gamma}_{i,i}\right)^2}(\mathbf{F}\boldsymbol{\mathscr{T}})_i\,\mathrm{Var}\left[\mathbf{d}_{\mathbf{y}}(t)\right](\mathbf{F}\boldsymbol{\mathscr{T}})_i^{\mathrm{T}} \\
&\quad +2\frac{h\boldsymbol{\Gamma}_{i,i}\gamma_q(1-h\boldsymbol{\Gamma}_{i,i},1-h\boldsymbol{\Gamma}_{i,i},n)}{1-\left(1-h\boldsymbol{\Gamma}_{i,i}\right)^2}\mathrm{Cov}\left[d_{x_i}(t)+\boldsymbol{\Gamma}_{i,i}^{-1}d_{\tilde{\beta}_{a,i}}(t),\mathbf{d}_{\mathbf{y}}(t)\right](\mathbf{F}\boldsymbol{\mathscr{T}})_i^{\mathrm{T}}, \\
&\quad i=1,\ldots,n_x,
\end{aligned}
\tag{E.24}
$$

assuming that the noise in $\tilde{\mathbf{U}}_a(t)$ is negligible.

E.3 Proof of Proposition 6.3

First of all, note that

$$
\lim_{h\to 0}\mathbf{M}_x^{\tau/h}=\left(\lim_{h\to 0}\left(\mathbf{I}_{n_x}+h^{-1}\left(\mathbf{M}_x-\mathbf{I}_{n_x}\right)h\right)^{1/h}\right)^{\tau}=\exp\left(\lim_{h\to 0}h^{-1}\left(\mathbf{M}_x-\mathbf{I}_{n_x}\right)\right)^{\tau}. \tag{E.25}
$$

Hence, as a consequence of Appendix E.2, if the condition in Eq. (6.58) is satisfied, then

$$\begin{aligned}\lim_{h\to 0}\mathbf{x}(t)-\mathbf{x}^s(t) &= \exp\left(nh\lim_{h\to 0}h^{-1}\left(\mathbf{M}_x-\mathbf{I}_{n_x}\right)\right)\left(\mathbf{x}(t-nh)-\mathbf{x}^s(t-nh)\right)\\ &\quad+\lim_{h\to 0}\sum_{m=1}^{n}\exp\left((m-1)h\lim_{h\to 0}h^{-1}\left(\mathbf{M}_x-\mathbf{I}_{n_x}\right)\right)\boldsymbol{\upsilon}_x(t-mh)\\ &= \exp\left(nh\left(-\boldsymbol{\Gamma}\right)\right)\left(\mathbf{x}(t-nh)-\mathbf{x}^s(t-nh)\right)\\ &\quad+\int_0^{nh}\exp\left(\tau\left(-\boldsymbol{\Gamma}\right)\right)\lim_{h\to 0}h^{-1}\boldsymbol{\upsilon}_x(t-\tau)\mathrm{d}\tau. \end{aligned}\tag{E.26}$$

Since $\mathbf{I}_{n_x}-h\boldsymbol{\Gamma}$ is the matrix of eigenvalues of $\mathbf{M}_x$, for each eigenvalue

$$\lambda_i = 1-h\boldsymbol{\Gamma}_{i,i},\quad i=1,\ldots,n_x,\tag{E.27}$$

the following result is verified:

$$\lim_{h\to 0}\frac{\lambda_i-1}{h}=-\boldsymbol{\Gamma}_{i,i},\quad i=1,\ldots,n_x,\tag{E.28}$$

with $\boldsymbol{\Gamma}_{i,i}>0$.

This shows that the condition in Eq. (5.23) is also satisfied. Since this is a sufficient condition for Eqs. (5.24) and (5.25), the result is that

$$\lim_{h\to 0}\sigma^2_{x_i}=0,\quad i=1,\ldots,n_x.\tag{E.29}$$

Moreover, since $\mathbf{r}_u$ is Lipschitz continuous and the noise in $\tilde{\mathbf{U}}_a(t)$ is negligible,

$$\begin{aligned}\lim_{h\to 0}h^{-1}\boldsymbol{\upsilon}_x(t) &= \lim_{h\to 0}\mathbf{F}\mathscr{R}_q(\mathbf{r}_u,t)+\lim_{h\to 0}h\mathbf{F}\int_0^1(1-\xi)\dot{\mathbf{r}}_u(t+\xi h)\mathrm{d}\xi\\ &\quad-\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_\mathbf{y},t)-\boldsymbol{\Gamma}\mathbf{d}_\mathbf{x}(t)-\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t)\\ &= -\mathbf{F}\mathscr{T}\mathscr{D}_q(\mathbf{d}_\mathbf{y},t)-\boldsymbol{\Gamma}\mathbf{d}_\mathbf{x}(t)-\mathbf{d}_{\tilde{\boldsymbol{\beta}}_a}(t),\end{aligned}\tag{E.30}$$

which results in

$$\begin{aligned}\lim_{h\to 0}\mathrm{E}\left[\dot{\mathbf{x}}(t)\right] &= \lim_{h\to 0}\mathrm{E}\left[\frac{\mathbf{x}(t+h)-\mathbf{x}(t)}{h}\right]=\frac{\mathbf{x}^s(t+h)-\mathbf{x}^s(t)}{h}+\boldsymbol{\Gamma}\left(\mathbf{x}^s(t)-\mathbf{x}(t)\right)\\ &= \mathrm{E}\left[\mathbf{v}(t)\right]\end{aligned}\tag{E.31}$$

and

$$\lim_{h\to 0}\mathrm{E}\left[\mathbf{x}(t)-\mathbf{x}^s(t)\right]=\exp\left(-nh\boldsymbol{\Gamma}\right)\left(\mathbf{x}(t-nh)-\mathbf{x}^s(t-nh)\right).\tag{E.32}$$

F Appendix of Chapter 7

F.1 Proof of Proposition 7.2

At steady state at time t_k, one can assume $\tilde{\mathbf{x}}(t_k) = \mathbf{x}^s(t_k) = \bar{\mathbf{x}}_k$. The feedback control laws in Eqs. (7.19)–(7.20) then give:

$$\bar{\mathbf{u}}_k = -\mathbf{B}_a(\bar{\mathbf{x}}_k)^{-1}\Big(\mathbf{F}\hat{\bar{\mathbf{r}}}_{u,k} + \boldsymbol{\beta}_a(\bar{\mathbf{x}}_k)\Big). \tag{F.1}$$

Since the estimate of the slow states at steady state is

$$\begin{aligned}\hat{\bar{\mathbf{z}}}_k &= \mathbf{s}(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k, \hat{\bar{\mathbf{r}}}_{u,k}) \\ &= \mathbf{s}\Big(\bar{\mathbf{x}}_k, -\mathbf{B}_a(\bar{\mathbf{x}}_k)^{-1}\mathbf{F}\hat{\bar{\mathbf{r}}}_{u,k} - \mathbf{B}_a(\bar{\mathbf{x}}_k)^{-1}\boldsymbol{\beta}_a(\bar{\mathbf{x}}_k), \hat{\bar{\mathbf{r}}}_{u,k}\Big),\end{aligned} \tag{F.2}$$

and the only variable subject to the effect of noise is $\hat{\bar{\mathbf{r}}}_{u,k}$, the variance of the estimate $\hat{\bar{\mathbf{z}}}_k$ is given by:

$$\begin{aligned}\mathrm{Var}\left[\hat{\bar{\mathbf{z}}}_k\right] = \frac{\partial \mathbf{s}}{\partial \bar{\mathbf{u}}_k}(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k, \hat{\bar{\mathbf{r}}}_{u,k})\,\mathbf{B}_a(\bar{\mathbf{x}}_k)^{-1}\,\mathbf{F}\,\mathrm{Var}\left[\hat{\bar{\mathbf{r}}}_{u,k}\right]\,\mathbf{F}^{\mathrm{T}}\left(\mathbf{B}_a(\bar{\mathbf{x}}_k)^{-1}\right)^{\mathrm{T}}\,\frac{\partial \mathbf{s}}{\partial \bar{\mathbf{u}}_k}(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k, \hat{\bar{\mathbf{r}}}_{u,k})^{\mathrm{T}} \\ + \frac{\partial \mathbf{s}}{\partial \hat{\bar{\mathbf{r}}}_{u,k}}(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k, \hat{\bar{\mathbf{r}}}_{u,k})\,\mathrm{Var}\left[\hat{\bar{\mathbf{r}}}_{u,k}\right]\,\frac{\partial \mathbf{s}}{\partial \hat{\bar{\mathbf{r}}}_{u,k}}(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k, \hat{\bar{\mathbf{r}}}_{u,k})^{\mathrm{T}}.\end{aligned} \tag{F.3}$$

In particular, if

$$\mathbf{s}(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k, \hat{\bar{\mathbf{r}}}_{u,k}) = -\mathbf{H}_a(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k)^{-1}\,\mathbf{H}\,\hat{\bar{\mathbf{r}}}_{u,k}, \tag{F.4}$$

then

$$\frac{\partial \mathbf{s}}{\partial \bar{u}_{j,k}}(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k, \hat{\bar{\mathbf{r}}}_{u,k}) = \mathbf{H}_a(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k)^{-1} \frac{\partial \mathbf{H}_a}{\partial \bar{u}_{j,k}}(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k) \mathbf{H}_a(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k)^{-1} \mathbf{H} \hat{\bar{\mathbf{r}}}_{u,k}$$
$$= -\mathbf{H}_a(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k)^{-1} \frac{\partial \mathbf{H}_a}{\partial \bar{u}_{j,k}}(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k) \hat{\bar{\mathbf{z}}}_k, \qquad \forall j = 1, \ldots, n_u, \tag{F.5}$$

$$\frac{\partial \mathbf{s}}{\partial \hat{\bar{\mathbf{r}}}_{u,k}}(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k, \hat{\bar{\mathbf{r}}}_{u,k}) = -\mathbf{H}_a(\bar{\mathbf{x}}_k, \bar{\mathbf{u}}_k)^{-1} \mathbf{H}. \tag{F.6}$$

G Appendix of Chapter 8

G.1 Adjoint-free Optimal Control Laws for Reactors

G.1.1 One independent reaction

One can show that

$$\begin{aligned}\det\left(\mathscr{M}_j\right) &= \det\left(\left[\tfrac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u}) \;\; \Delta_j \tfrac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u})\right]\right)\\ &= \det\left(\begin{bmatrix} 0 & -\frac{\partial r_v}{\partial x_j} \\ 1 & \omega \end{bmatrix}\right)\\ &= \frac{\partial r_v}{\partial x_j}, \end{aligned} \tag{G.1}$$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\left(\det\left(\mathscr{M}_j\right)\right) &= \frac{\partial}{\partial \mathbf{x}}\left(\frac{\partial r_v}{\partial x_j}\right)\mathbf{f}(\mathbf{x},\mathbf{u})\\ &= \frac{\partial}{\partial \check{\mathbf{x}}_j}\left(\frac{\partial r_v}{\partial x_j}\right)\check{\mathbf{f}}_j(\mathbf{x},\mathbf{u}) + \frac{\partial}{\partial x_j}\left(\frac{\partial r_v}{\partial x_j}\right)\left(u_j - \omega x_j\right). \end{aligned} \tag{G.2}$$

G.1.2 Two independent reactions

One can show that

$$\begin{aligned}
\det\left(\mathscr{M}_j\right) &= \det\left(\left[\tfrac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u}) \;\; \Delta_j \tfrac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u}) \;\; \Delta_j^2 \tfrac{\partial \mathbf{f}^{u_j}}{\partial u_j}(\mathbf{x},\mathbf{u})\right]\right) \\
&= \det\left(\begin{bmatrix} \mathbf{0}_R & -\frac{\partial \mathbf{r}_v}{\partial x_j} & \left(\frac{\partial \mathbf{r}_v}{\partial \mathbf{x}_r} - 2\omega \mathbf{I}_R\right)\frac{\partial \mathbf{r}_v}{\partial x_j} - \frac{\partial}{\partial \check{\mathbf{x}}_j}\left(\frac{\partial \mathbf{r}_v}{\partial x_j}\right)\check{\mathbf{f}}_j(\mathbf{x},\mathbf{u}) \\ 1 & \omega & \omega^2 \end{bmatrix}\right) \\
&\quad + \det\left(\begin{bmatrix} \mathbf{0}_R & -\frac{\partial \mathbf{r}_v}{\partial x_j} & -\frac{\partial}{\partial x_j}\left(\frac{\partial \mathbf{r}_v}{\partial x_j}\right)\left(u_j - \omega x_j\right) \\ 1 & \omega & 0 \end{bmatrix}\right) \\
&= \det\left(\left[\tfrac{\partial \mathbf{r}_v}{\partial x_j} \;\; \tfrac{\partial}{\partial \check{\mathbf{x}}_j}\left(\tfrac{\partial \mathbf{r}_v}{\partial x_j}\right)\check{\mathbf{f}}_j(\mathbf{x},\mathbf{u}) - \left(\tfrac{\partial \mathbf{r}_v}{\partial \mathbf{x}_r} - 2\omega \mathbf{I}_R\right)\tfrac{\partial \mathbf{r}_v}{\partial x_j}\right]\right) \\
&\quad + \det\left(\left[\tfrac{\partial \mathbf{r}_v}{\partial x_j} \;\; \tfrac{\partial}{\partial x_j}\left(\tfrac{\partial \mathbf{r}_v}{\partial x_j}\right)\right]\right)\left(u_j - \omega x_j\right).
\end{aligned} \tag{G.3}$$

G.2 Arc Sequences with Active Pure-state Path Constraints

If a pure-state path constraint becomes active, the choice of the new feedback laws for the inputs is made according to a set of rules that specify the feedback laws by taking into account the path constraint that becomes active and the correspondence between each path constraint that was active and the input that was being adjusted to make it remain active before the effective switching time. In particular, some constraints can already be active when the feedback laws are initialized according to the arc that was specified for the interval that starts at t_i. If there is a pure-state path constraint such that $h_k\left(\mathbf{x}(t_i)\right) = 0 \wedge h_k^{(1)}\left(\mathbf{x}(t_i),\mathbf{u}(t_i)\right) > 0$, for some $k = 1,\ldots,n_h$, the set of rules that was mentioned above is used to determine a new set of feedback laws. The process is repeated until there are no such path constraints.

The changes in the arc sequence due to pure-state path constraints imply that the degree $\xi_{j,i}$ for which a feedback law explicitly gives $u_j^{(\xi_{j,i})}(t)$ as a function of the states, the inputs, and the time derivatives of the inputs may not be constant for all $j = 1,\ldots,n_u$. Nevertheless, at least it is known that this degree cannot increase, because the new feedback laws are always static rather than dynamic.

Hence, let us suppose that, in the interval $\left[t_{i-1}, t_i\right)$, there are $\tilde{n}_i$ switchings to different arcs of type 2, and let us describe the arcs in the r_ith subinterval $t \in \left[t_{i,r_i-1}, t_{i,r_i}\right)$, for some $r_i = 1,\ldots,\tilde{n}_i + 1$, where $t_{i,0}$ corresponds to t_{i-1} and $t_{i,\tilde{n}_i+1}$ corresponds to t_i. For each input u_j, with $j = 1,\ldots,n_u$, there is a degree ξ_{j,i,r_i} for which a feedback law explicitly gives $u_j^{(\xi_{j,i,r_i})}(t)$ as a function of the states, the inputs, and the time derivatives of the inputs, as

follows:

$$u_j^{(\xi_{j,i,r_i})}(t) = c_{j,i,r_i}\left(\mathbf{x}(t), \mathbf{p}_{j,i}, u_1^{(\xi_{1,i,r_i}-1)}(t), \ldots, u_1(t), \ldots, u_{n_u}^{(\xi_{n_u,i,r_i}-1)}(t), \ldots, u_{n_u}(t)\right), \tag{G.4}$$

with

$$\begin{aligned} \dot{u}_j^{(\xi_{j,i,r_i}-1)}(t) &= u_j^{(\xi_{j,i,r_i})}(t), \quad u_j^{(\xi_{j,i,r_i}-1)}(t_{i,r_i-1}) = \tilde{u}_{j,i}^{\xi_{j,i,r_i}-1}(t_{i,r_i-1}), \\ &\vdots \\ \dot{u}_j(t) &= u_j^{(1)}(t), \qquad\qquad u_j(t_{i,r_i-1}) = \tilde{u}_{j,i}^{0}(t_{i,r_i-1}). \end{aligned} \tag{G.5}$$

Then, it is possible to write that, for all $i = 1, \ldots, n_s+1$, for all $r_i = 1, \ldots, \tilde{n}_i+1$, and for all $t \in \left[t_{i,r_i-1}, t_{i,r_i}\right)$,

$$\mathbf{q}_i\left(\mathbf{x}(t), \mathbf{z}_i(t)\right) = \begin{bmatrix} \mathbf{0}_{b_{1,i}\pi_i+\xi_{1,i}-\xi_{1,i,r_i}} \\ c_{1,i,r_i}\left(\mathbf{x}(t), \mathbf{z}_i(t)\right) \\ \vdots \\ \tilde{u}_{1,i}^{1}(t) \\ \vdots \\ \mathbf{0}_{b_{n_u,i}\pi_i+\xi_{n_u,i}-\xi_{n_u,i,r_i}} \\ c_{n_u,i,r_i}\left(\mathbf{x}(t), \mathbf{z}_i(t)\right) \\ \vdots \\ \tilde{u}_{n_u,i}^{1}(t) \end{bmatrix}, \tag{G.6}$$

and, for all $i = 1, \ldots, n_s+1$, and for all $t \notin \left[t_{i-1}, t_i\right)$,

$$\mathbf{q}_i\left(\mathbf{x}(t), \mathbf{z}_i(t)\right) = \mathbf{0}_{n_{z,i}}. \tag{G.7}$$

Then, for the complete arc sequence, one uses the control laws

$$\mathbf{u}(t) = \tilde{\mathbf{c}}\left(\mathbf{z}(t)\right), \tag{G.8}$$

where, for all $j = 1, \ldots, n_u$, for all $i = 1, \ldots, n_s+1$, for all $r_i = 1, \ldots, \tilde{n}_i+1$, and for all $t \in \left[t_{i,r_i-1}, t_{i,r_i}\right)$,

$$\tilde{c}_j\left(\mathbf{z}(t)\right) = \begin{cases} \tilde{u}_{j,i}^{0}(t), & \text{if } \xi_{j,i,r_i} > 0 \\ c_{j,i,r_i}\left(\mathbf{x}(t), \mathbf{z}_i(t)\right), & \text{if } \xi_{j,i,r_i} = 0 \end{cases}. \tag{G.9}$$

G.3 Checking the PMP Conditions

The necessary conditions of optimality for Problem (8.57) are the following:

1. The switching times $t_1^*, \ldots, t_{n_s}^*$ and the initial conditions $\mathbf{z}_{1,0}^*, \ldots, \mathbf{z}_{n_s+1,0}^*$ satisfy the conditions

$$\begin{aligned}
&\frac{\partial \hat{\mathscr{J}}}{\partial t_i}(\bar{\mathbf{u}}^*(\cdot), t_1^*, \ldots, t_{n_s}^*, t_f^*, \mathbf{z}_{1,0}^*, \ldots, \mathbf{z}_{n_s+1,0}^*)^{\mathrm{T}} \\
&\quad + \begin{bmatrix} \frac{\partial \hat{\theta}}{\partial t_i}(\bar{\mathbf{u}}^*(\cdot), t_1^*, \ldots, t_{n_s}^*, t_f^*, \mathbf{z}_{1,0}^*, \ldots, \mathbf{z}_{n_s+1,0}^*) \\ \frac{\partial \hat{\mathscr{T}}}{\partial t_i}(\bar{\mathbf{u}}^*(\cdot), t_1^*, \ldots, t_{n_s}^*, t_f^*, \mathbf{z}_{1,0}^*, \ldots, \mathbf{z}_{n_s+1,0}^*) \end{bmatrix}^{\mathrm{T}} \begin{bmatrix} \bar{\xi}^* \\ \bar{\nu}^* \end{bmatrix} = 0, \\
&\quad \forall i = 1, \ldots, n_s, \qquad \text{(G.10)} \\
&\frac{\partial \hat{\mathscr{J}}}{\partial \mathbf{z}_{i,0}}(\bar{\mathbf{u}}^*(\cdot), t_1^*, \ldots, t_{n_s}^*, t_f^*, \mathbf{z}_{1,0}^*, \ldots, \mathbf{z}_{n_s+1,0}^*)^{\mathrm{T}} \\
&\quad + \begin{bmatrix} \frac{\partial \hat{\theta}}{\partial \mathbf{z}_{i,0}}(\bar{\mathbf{u}}^*(\cdot), t_1^*, \ldots, t_{n_s}^*, t_f^*, \mathbf{z}_{1,0}^*, \ldots, \mathbf{z}_{n_s+1,0}^*) \\ \frac{\partial \hat{\mathscr{T}}}{\partial \mathbf{z}_{i,0}}(\bar{\mathbf{u}}^*(\cdot), t_1^*, \ldots, t_{n_s}^*, t_f^*, \mathbf{z}_{1,0}^*, \ldots, \mathbf{z}_{n_s+1,0}^*) \end{bmatrix}^{\mathrm{T}} \begin{bmatrix} \bar{\xi}^* \\ \bar{\nu}^* \end{bmatrix} = \mathbf{0}_{n_{z,i}}, \\
&\quad \forall i = 1, \ldots, n_s + 1. \qquad \text{(G.11)}
\end{aligned}$$

2. The states $\bar{\mathbf{x}}^*(t)$ are continuous at each instant $t \in \left[t_0, t_f^*\right]$, and the differential equations of the states

$$\dot{\bar{\mathbf{x}}}^*(t) = \bar{\mathbf{f}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big) \qquad \text{(G.12)}$$

are satisfied at each instant $t \in \left[t_0, t_f^*\right]$ that is not an effective switching time, with the initial conditions

$$\bar{\mathbf{x}}^*(t_0) = \bar{\mathbf{x}}_0. \qquad \text{(G.13)}$$

3. The adjoint variables $\bar{\boldsymbol{\lambda}}^*(t)$ are continuous at each instant $t \in \left[t_0, t_f^*\right]$ that is not an entry point, the differential equations of the adjoint variables

$$\begin{aligned}
\dot{\bar{\boldsymbol{\lambda}}}^*(t) = &-\frac{\partial \bar{\mathbf{f}}}{\partial \bar{\mathbf{x}}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big)^{\mathrm{T}} \bar{\boldsymbol{\lambda}}^*(t) \\
&- \frac{\partial \bar{\mathbf{g}}}{\partial \bar{\mathbf{x}}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big)^{\mathrm{T}} \bar{\boldsymbol{\mu}}^*(t) - \frac{\partial \bar{\mathbf{h}}^{(1)}}{\partial \bar{\mathbf{x}}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big)^{\mathrm{T}} \bar{\boldsymbol{\eta}}^*(t) \qquad \text{(G.14)}
\end{aligned}$$

are satisfied at each instant $t \in \left[t_0, t_f^*\right]$ that is not an effective switching time, the transversal conditions

$$\bar{\boldsymbol{\lambda}}^*(t_f^*) = \frac{\partial \bar{\phi}}{\partial \bar{\mathbf{x}}}\big(\bar{\mathbf{x}}^*(t_f^*), t_f^*\big)^{\mathrm{T}} + \begin{bmatrix} \frac{\partial \bar{\boldsymbol{\omega}}}{\partial \bar{\mathbf{x}}}\big(\bar{\mathbf{x}}^*(t_f^*), t_f^*\big) \\ \frac{\partial \bar{\psi}}{\partial \bar{\mathbf{x}}}\big(\bar{\mathbf{x}}^*(t_f^*), t_f^*\big) \end{bmatrix}^{\mathrm{T}} \begin{bmatrix} \bar{\xi}^* \\ \bar{\nu}^* \end{bmatrix} \qquad \text{(G.15)}$$

are satisfied at the terminal time, and the conditions

$$\bar{\boldsymbol{\lambda}}^*(\theta^-) = \bar{\boldsymbol{\lambda}}^*(\theta) + \frac{\partial \bar{\mathbf{h}}}{\partial \bar{\mathbf{x}}}\big(\bar{\mathbf{x}}^*(\theta^-)\big)^{\mathrm{T}} \bar{\boldsymbol{\pi}}^*(\theta) \tag{G.16}$$

are satisfied at each entry point θ, where the n_h-dimensional vector of Lagrange multipliers $\bar{\boldsymbol{\pi}}^*(\theta)$ satisfies the conditions

$$\bar{\boldsymbol{\pi}}^*(\theta) \geq \bar{\boldsymbol{\eta}}^*(\theta), \tag{G.17}$$

$$\bar{h}_k\big(\bar{\mathbf{x}}^*(\theta)\big)\bar{\pi}_k^*(\theta) = 0, \quad \forall k = 1, \ldots, n_h. \tag{G.18}$$

4. The reformulated Hamiltonian function, defined as

$$\begin{aligned}\bar{\mathscr{H}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t), \bar{\boldsymbol{\lambda}}^*(t), t_f^*, \bar{\mathbf{x}}^*(t_f^*), \bar{\boldsymbol{\xi}}^*, \bar{\boldsymbol{\nu}}^*\big) := {} & \bar{\mathbf{f}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big)^{\mathrm{T}} \bar{\boldsymbol{\lambda}}^*(t) \\ & + \frac{\partial \bar{\phi}}{\partial t}\big(\bar{\mathbf{x}}^*(t_f^*), t_f^*\big)^{\mathrm{T}} \\ & + \begin{bmatrix} \frac{\partial \bar{\boldsymbol{\omega}}}{\partial t}\big(\bar{\mathbf{x}}^*(t_f^*), t_f^*\big) \\ \frac{\partial \bar{\boldsymbol{\psi}}}{\partial t}\big(\bar{\mathbf{x}}^*(t_f^*), t_f^*\big) \end{bmatrix}^{\mathrm{T}} \begin{bmatrix} \bar{\boldsymbol{\xi}}^* \\ \bar{\boldsymbol{\nu}}^* \end{bmatrix},\end{aligned} \tag{G.19}$$

satisfies the condition

$$\bar{\mathscr{H}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t), \bar{\boldsymbol{\lambda}}^*(t), t_f^*, \bar{\mathbf{x}}^*(t_f^*), \bar{\boldsymbol{\xi}}^*, \bar{\boldsymbol{\nu}}^*\big) = 0 \tag{G.20}$$

at each instant $t \in \left[t_0, t_f^*\right]$.

5. The conditions

$$\bar{\boldsymbol{\omega}}\big(\bar{\mathbf{x}}^*(t_f^*), t_f^*\big) = \mathbf{0}_{n_\omega}, \tag{G.21}$$

$$\bar{\boldsymbol{\psi}}\big(\bar{\mathbf{x}}^*(t_f^*), t_f^*\big) \leq \mathbf{0}_{n_\psi}, \tag{G.22}$$

$$\bar{\boldsymbol{\nu}}^* \geq \mathbf{0}_{n_\psi}, \tag{G.23}$$

$$\bar{\psi}_k\big(\bar{\mathbf{x}}^*(t_f^*), t_f^*\big)\bar{\nu}_k^* = 0, \quad \forall k = 1, \ldots, n_\psi, \tag{G.24}$$

are satisfied.

6. The Lagrangian function, defined as

$$\begin{aligned}\bar{\mathscr{L}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t), \bar{\boldsymbol{\lambda}}^*(t), \bar{\boldsymbol{\mu}}^*(t), \bar{\boldsymbol{\eta}}^*(t)\big) := {} & \bar{\mathbf{f}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big)^{\mathrm{T}} \bar{\boldsymbol{\lambda}}^*(t) \\ & + \bar{\mathbf{g}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big)^{\mathrm{T}} \bar{\boldsymbol{\mu}}^*(t) \\ & + \bar{\mathbf{h}}^{(1)}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big)^{\mathrm{T}} \bar{\boldsymbol{\eta}}^*(t),\end{aligned} \tag{G.25}$$

satisfies the stationarity conditions

$$\begin{aligned}\mathbf{0}_{n_u} &= \frac{\partial \mathscr{L}}{\partial \bar{\mathbf{u}}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t), \bar{\boldsymbol{\lambda}}^*(t), \bar{\boldsymbol{\mu}}^*(t), \bar{\boldsymbol{\eta}}^*(t)\big)^{\mathrm{T}} \\ &= \frac{\partial \bar{\mathbf{f}}}{\partial \bar{\mathbf{u}}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big)^{\mathrm{T}} \bar{\boldsymbol{\lambda}}^*(t) \\ &\quad + \frac{\partial \bar{\mathbf{g}}}{\partial \bar{\mathbf{u}}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big)^{\mathrm{T}} \bar{\boldsymbol{\mu}}^*(t) + \frac{\partial \bar{\mathbf{h}}^{(1)}}{\partial \bar{\mathbf{u}}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big)^{\mathrm{T}} \bar{\boldsymbol{\eta}}^*(t) \end{aligned} \tag{G.26}$$

at each instant $t \in \left[t_0, t_f^*\right]$.

7. The conditions

$$\bar{\mathbf{g}}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big) \leq \mathbf{0}_{n_g}, \tag{G.27}$$

$$\bar{\boldsymbol{\mu}}^*(t) \geq \mathbf{0}_{n_g}, \tag{G.28}$$

$$\bar{g}_k\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big)\bar{\mu}_k^*(t) = 0, \quad \forall k = 1, \ldots, n_g, \tag{G.29}$$

are satisfied at each instant $t \in \left[t_0, t_f^*\right]$.

8. The conditions

$$\bar{\mathbf{h}}\big(\bar{\mathbf{x}}^*(t)\big) \leq \mathbf{0}_{n_h}, \tag{G.30}$$

$$\bar{h}_k\big(\bar{\mathbf{x}}^*(t)\big) < 0 \vee \bar{h}_k^{(1)}\big(\bar{\mathbf{x}}^*(t), \bar{\mathbf{u}}^*(t)\big) \leq 0, \quad \forall k = 1, \ldots, n_h, \tag{G.31}$$

$$\bar{\boldsymbol{\eta}}^*(t) \geq \mathbf{0}_{n_h}, \tag{G.32}$$

$$\dot{\bar{\boldsymbol{\eta}}}^*(t) \leq \mathbf{0}_{n_h}, \tag{G.33}$$

$$\bar{h}_k\big(\bar{\mathbf{x}}^*(t)\big)\bar{\eta}_k^*(t) = 0, \quad \forall k = 1, \ldots, n_h, \tag{G.34}$$

are satisfied at each instant $t \in \left[t_0, t_f^*\right]$.

Now, let us investigate how these conditions can be checked from the solution to Problem (8.40). First of all, let us note that the conditions in Eqs. (G.12), (G.13), (G.21), (G.22), (G.27), (G.30) and (G.31) are necessarily satisfied for any feasible solution. Moreover, upon convergence of numerical optimization, the values of the decision variables $t_1^*, \ldots, t_{n_s}^*$, t_f^*, $\mathbf{z}_{1,0}^*, \ldots, \mathbf{z}_{n_s+1,0}^*$ and of the Lagrange multipliers $\bar{\boldsymbol{\xi}}^*$ and $\bar{\boldsymbol{\nu}}^*$ that correspond to the terminal

constraints in Eqs. (G.21) and (G.22), respectively, are such that the conditions

$$\begin{aligned}&\frac{\partial \hat{\phi}}{\partial t_i}(t_1^*,\ldots,t_{n_s}^*,t_f^*,\mathbf{z}_{1,0}^*,\ldots,\mathbf{z}_{n_s+1,0}^*)^{\mathrm{T}}\\&\quad+\begin{bmatrix}\frac{\partial \hat{\boldsymbol{\omega}}}{\partial t_i}(t_1^*,\ldots,t_{n_s}^*,t_f^*,\mathbf{z}_{1,0}^*,\ldots,\mathbf{z}_{n_s+1,0}^*)\\ \frac{\partial \hat{\boldsymbol{\psi}}}{\partial t_i}(t_1^*,\ldots,t_{n_s}^*,t_f^*,\mathbf{z}_{1,0}^*,\ldots,\mathbf{z}_{n_s+1,0}^*)\end{bmatrix}^{\mathrm{T}}\begin{bmatrix}\bar{\boldsymbol{\xi}}^*\\ \bar{\boldsymbol{\nu}}^*\end{bmatrix}=0,\quad \forall i=1,\ldots,n_s,\end{aligned}\tag{G.35}$$

$$\begin{aligned}&\frac{\partial \hat{\phi}}{\partial \mathbf{z}_{i,0}^*}(t_1^*,\ldots,t_{n_s}^*,t_f^*,\mathbf{z}_{1,0}^*,\ldots,\mathbf{z}_{n_s+1,0}^*)^{\mathrm{T}}\\&\quad+\begin{bmatrix}\frac{\partial \hat{\boldsymbol{\omega}}}{\partial \mathbf{z}_{i,0}^*}(t_1^*,\ldots,t_{n_s}^*,t_f^*,\mathbf{z}_{1,0}^*,\ldots,\mathbf{z}_{n_s+1,0}^*)\\ \frac{\partial \hat{\boldsymbol{\psi}}}{\partial \mathbf{z}_{i,0}^*}(t_1^*,\ldots,t_{n_s}^*,t_f^*,\mathbf{z}_{1,0}^*,\ldots,\mathbf{z}_{n_s+1,0}^*)\end{bmatrix}^{\mathrm{T}}\begin{bmatrix}\bar{\boldsymbol{\xi}}^*\\ \bar{\boldsymbol{\nu}}^*\end{bmatrix}=\mathbf{0}_{n_{z,i}},\quad \forall i=1,\ldots,n_s+1,\end{aligned}\tag{G.36}$$

are satisfied, which ensures that the conditions in Eqs. (G.10) and (G.11) are also satisfied.

Then, if $\mathbf{u}^*(t)$ is adjusted to ensure that the path constraints are satisfied, one can also show that

$$\frac{\partial \bar{g}_k}{\partial \bar{\mathbf{x}}}(\bar{\mathbf{x}}^*(t),\mathbf{0}_{n_u})^{\mathrm{T}}\bar{\mu}_k^*(t)=\mathbf{0}_{n_z},\quad \forall k=1,\ldots,n_g,\tag{G.37}$$

$$\frac{\partial \bar{h}_k^{(1)}}{\partial \bar{\mathbf{x}}}(\bar{\mathbf{x}}^*(t),\mathbf{0}_{n_u})^{\mathrm{T}}\bar{\eta}_k^*(t)=\mathbf{0}_{n_z},\quad \forall k=1,\ldots,n_h,\tag{G.38}$$

at each instant $t\in\left[t_0,t_f^*\right]$.

The first set of equalities above is valid because, either $\bar{\mu}_k^*(t)$ is equal to zero due to the fact that the corresponding constraint $\bar{g}_k(\bar{\mathbf{x}}^*(t),\mathbf{0}_{n_u})\leq 0$ is inactive, or the constraint is active and $\mathbf{u}^*(t)$ is adjusted according to $\bar{\mathbf{x}}^*(t)$ such that $\bar{g}_k(\bar{\mathbf{x}}^*(t),\mathbf{0}_{n_u})$ remains identically equal to zero until the next effective switching time, leading $\frac{\partial \bar{g}_k}{\partial \bar{\mathbf{x}}}(\bar{\mathbf{x}}^*(t),\mathbf{0}_{n_u})$ to be equal to zero as well.

The second set of equalities above is valid because, either $\bar{\eta}_k^*(t)$ is equal to zero due to the fact that the corresponding constraint $\bar{h}_k\big(\bar{\mathbf{x}}^*(t)\big)\leq 0$ is inactive, or the constraint is active and $\mathbf{u}^*(t)$ is adjusted according to $\bar{\mathbf{x}}^*(t)$ such that both $\bar{h}_k\big(\bar{\mathbf{x}}^*(t)\big)$ and its time derivative $\bar{h}_k^{(1)}(\bar{\mathbf{x}}^*(t),\mathbf{0}_{n_u})$ remain identically equal to zero until the next effective switching time, leading $\frac{\partial \bar{h}_k^{(1)}}{\partial \bar{\mathbf{x}}}(\bar{\mathbf{x}}^*(t),\mathbf{0}_{n_u})$ to be equal to zero as well.

This means that, if

$$\dot{\bar{\boldsymbol{\lambda}}}^*(t)=-\frac{\partial \bar{\mathbf{f}}}{\partial \bar{\mathbf{x}}}(\bar{\mathbf{x}}^*(t),\mathbf{0}_{n_u})^{\mathrm{T}}\bar{\boldsymbol{\lambda}}^*(t)\tag{G.39}$$

is satisfied at each instant $t\in\left[t_0,t_f^*\right]$ that is not an effective switching time, then Eq. (G.14) also holds.

Furthermore, if one considers the adjoint variables

$$\bar{\boldsymbol{\lambda}}^*(t) = \bar{\boldsymbol{\lambda}}^*_{\bar{\phi}}(t) + \left[\bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\omega}}}(t) \;\; \bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\psi}}}(t)\right] \begin{bmatrix} \bar{\boldsymbol{\xi}}^* \\ \bar{\boldsymbol{\nu}}^* \end{bmatrix}, \tag{G.40}$$

and the Lagrange multipliers

$$\bar{\boldsymbol{\pi}}^*(\theta) = \bar{\boldsymbol{\pi}}^*_{\bar{\phi}}(\theta) + \left[\bar{\boldsymbol{\pi}}^*_{\bar{\boldsymbol{\omega}}}(\theta) \;\; \bar{\boldsymbol{\pi}}^*_{\bar{\boldsymbol{\psi}}}(\theta)\right] \begin{bmatrix} \bar{\boldsymbol{\xi}}^* \\ \bar{\boldsymbol{\nu}}^* \end{bmatrix} \tag{G.41}$$

at each entry point θ, where $\bar{\boldsymbol{\lambda}}^*_{\bar{\phi}}(t)$, $\bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\omega}}}(t)$ and $\bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\psi}}}(t)$ are the adjoint variables that were computed for the solution to the problem, these variables satisfy, for each $\bar{\chi} \in \left\{\bar{\phi}, \bar{\boldsymbol{\omega}}, \bar{\boldsymbol{\psi}}\right\}$,

$$\bar{\boldsymbol{\lambda}}^*_{\bar{\chi}}(\theta^-) = \bar{\boldsymbol{\lambda}}^*_{\bar{\chi}}(\theta) + \frac{\partial \bar{\mathbf{h}}}{\partial \bar{\mathbf{x}}}\left(\bar{\mathbf{x}}^*(\theta^-)\right)^{\mathrm{T}} \bar{\boldsymbol{\pi}}^*_{\bar{\chi}}(\theta), \tag{G.42}$$

with

$$\bar{\pi}^*_{\bar{\chi},k}(\theta) = \begin{cases} -\frac{\left(\bar{\mathbf{f}}(\bar{\mathbf{x}}^*(\theta^-),\mathbf{0}_{n_u}) - \bar{\mathbf{f}}(\bar{\mathbf{x}}^*(\theta),\mathbf{0}_{n_u})\right)^{\mathrm{T}} \bar{\boldsymbol{\lambda}}^*_{\bar{\chi}}(\theta)}{\bar{h}^{(1)}_k(\bar{\mathbf{x}}^*(\theta^-),\mathbf{0}_{n_u})}, & \bar{h}_k\left(\bar{\mathbf{x}}^*(\theta)\right) = \bar{h}^{(1)}_k(\bar{\mathbf{x}}^*(\theta),\mathbf{0}_{n_u}) = 0 \\ 0, & \bar{h}_k\left(\bar{\mathbf{x}}^*(\theta)\right) < 0 \vee \bar{h}^{(1)}_k(\bar{\mathbf{x}}^*(\theta),\mathbf{0}_{n_u}) < 0 \end{cases}, \\ \forall k = 1,\ldots,n_h. \tag{G.43}$$

Then, the conditions in Eqs. (G.14), (G.15), (G.16) and (G.18) are necessarily satisfied since

$$\begin{aligned} \dot{\bar{\boldsymbol{\lambda}}}^*(t) &= \dot{\bar{\boldsymbol{\lambda}}}^*_{\bar{\phi}}(t) + \left[\dot{\bar{\boldsymbol{\lambda}}}^*_{\bar{\boldsymbol{\omega}}}(t) \;\; \dot{\bar{\boldsymbol{\lambda}}}^*_{\bar{\boldsymbol{\psi}}}(t)\right] \begin{bmatrix} \bar{\boldsymbol{\xi}}^* \\ \bar{\boldsymbol{\nu}}^* \end{bmatrix} \\ &= -\frac{\partial \bar{\mathbf{f}}}{\partial \bar{\mathbf{x}}}(\bar{\mathbf{x}}^*(t),\mathbf{0}_{n_u})^{\mathrm{T}} \left(\bar{\boldsymbol{\lambda}}^*_{\bar{\phi}}(t) + \left[\bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\omega}}}(t) \;\; \bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\psi}}}(t)\right] \begin{bmatrix} \bar{\boldsymbol{\xi}}^* \\ \bar{\boldsymbol{\nu}}^* \end{bmatrix}\right) \\ &= -\frac{\partial \bar{\mathbf{f}}}{\partial \bar{\mathbf{x}}}(\bar{\mathbf{x}}^*(t),\mathbf{0}_{n_u})^{\mathrm{T}} \bar{\boldsymbol{\lambda}}^*(t) \end{aligned} \tag{G.44}$$

for each instant $t \in \left[t_0, t_f^*\right]$ that is not an effective switching time,

$$\begin{aligned} \bar{\boldsymbol{\lambda}}^*(t_f^*) &= \bar{\boldsymbol{\lambda}}^*_{\bar{\phi}}(t_f^*) + \left[\bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\omega}}}(t_f^*) \;\; \bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\psi}}}(t_f^*)\right] \begin{bmatrix} \bar{\boldsymbol{\xi}}^* \\ \bar{\boldsymbol{\nu}}^* \end{bmatrix} \\ &= \frac{\partial \bar{\phi}}{\partial \bar{\mathbf{x}}}\left(\bar{\mathbf{x}}^*(t_f^*), t_f^*\right)^{\mathrm{T}} + \left[\frac{\partial \bar{\boldsymbol{\omega}}}{\partial \bar{\mathbf{x}}}\left(\bar{\mathbf{x}}^*(t_f^*), t_f^*\right)^{\mathrm{T}} \;\; \frac{\partial \bar{\boldsymbol{\psi}}}{\partial \bar{\mathbf{x}}}\left(\bar{\mathbf{x}}^*(t_f^*), t_f^*\right)^{\mathrm{T}}\right] \begin{bmatrix} \bar{\boldsymbol{\xi}}^* \\ \bar{\boldsymbol{\nu}}^* \end{bmatrix} \\ &= \frac{\partial \bar{\phi}}{\partial \bar{\mathbf{x}}}\left(\bar{\mathbf{x}}^*(t_f^*), t_f^*\right)^{\mathrm{T}} + \begin{bmatrix} \frac{\partial \bar{\boldsymbol{\omega}}}{\partial \bar{\mathbf{x}}}\left(\bar{\mathbf{x}}^*(t_f^*), t_f^*\right) \\ \frac{\partial \bar{\boldsymbol{\psi}}}{\partial \bar{\mathbf{x}}}\left(\bar{\mathbf{x}}^*(t_f^*), t_f^*\right) \end{bmatrix}^{\mathrm{T}} \begin{bmatrix} \bar{\boldsymbol{\xi}}^* \\ \bar{\boldsymbol{\nu}}^* \end{bmatrix} \end{aligned} \tag{G.45}$$

at the terminal time, and

$$\begin{aligned}\bar{\boldsymbol{\lambda}}^*(\theta^-) &= \bar{\boldsymbol{\lambda}}^*_{\bar{\phi}}(\theta^-) + \begin{bmatrix}\bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\omega}}}(\theta^-) & \bar{\boldsymbol{\lambda}}^*_{\bar{\psi}}(\theta^-)\end{bmatrix}\begin{bmatrix}\bar{\boldsymbol{\xi}}^*\\ \bar{\boldsymbol{\nu}}^*\end{bmatrix}\\ &= \bar{\boldsymbol{\lambda}}^*_{\bar{\phi}}(\theta) + \begin{bmatrix}\bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\omega}}}(\theta) & \bar{\boldsymbol{\lambda}}^*_{\bar{\psi}}(\theta)\end{bmatrix}\begin{bmatrix}\bar{\boldsymbol{\xi}}^*\\ \bar{\boldsymbol{\nu}}^*\end{bmatrix}\\ &\quad + \frac{\partial \bar{\mathbf{h}}}{\partial \bar{\mathbf{x}}}\big(\bar{\mathbf{x}}^*(\theta^-)\big)^{\mathrm{T}}\left(\bar{\boldsymbol{\pi}}^*_{\bar{\phi}}(\theta) + \begin{bmatrix}\bar{\boldsymbol{\pi}}^*_{\bar{\boldsymbol{\omega}}}(\theta) & \bar{\boldsymbol{\pi}}^*_{\bar{\psi}}(\theta)\end{bmatrix}\begin{bmatrix}\bar{\boldsymbol{\xi}}^*\\ \bar{\boldsymbol{\nu}}^*\end{bmatrix}\right)\\ &= \bar{\boldsymbol{\lambda}}^*(\theta) + \frac{\partial \bar{\mathbf{h}}}{\partial \bar{\mathbf{x}}}\big(\bar{\mathbf{x}}^*(\theta^-)\big)^{\mathrm{T}}\bar{\boldsymbol{\pi}}^*(\theta)\end{aligned} \tag{G.46}$$

and

$$\begin{aligned}\bar{h}_k\big(\bar{\mathbf{x}}^*(\theta)\big)\bar{\pi}^*_k(\theta) &= \bar{h}_k\big(\bar{\mathbf{x}}^*(\theta)\big)\left(\bar{\pi}^*_{\bar{\phi},k}(\theta) + \begin{bmatrix}\bar{\boldsymbol{\pi}}^*_{\bar{\boldsymbol{\omega}},k}(\theta) & \bar{\boldsymbol{\pi}}^*_{\bar{\psi},k}(\theta)\end{bmatrix}\begin{bmatrix}\bar{\boldsymbol{\xi}}^*\\ \bar{\boldsymbol{\nu}}^*\end{bmatrix}\right)\\ &= 0, \quad \forall k = 1,\ldots,n_h,\end{aligned} \tag{G.47}$$

at each entry point θ.

Then, for each instant $t \in \left[t_0, t_f^*\right]$, the condition in Eq. (G.20), written as

$$\begin{aligned}0 &= \bar{\mathbf{f}}\big(\bar{\mathbf{x}}^*(t),\bar{\mathbf{u}}^*(t)\big)^{\mathrm{T}}\bar{\boldsymbol{\lambda}}^*(t) + \frac{\partial \bar{\phi}}{\partial t}\big(\bar{\mathbf{x}}^*(t_f^*),t_f^*\big)^{\mathrm{T}} + \begin{bmatrix}\frac{\partial \bar{\boldsymbol{\omega}}}{\partial t}\big(\bar{\mathbf{x}}^*(t_f^*),t_f^*\big)\\ \frac{\partial \bar{\psi}}{\partial t}\big(\bar{\mathbf{x}}^*(t_f^*),t_f^*\big)\end{bmatrix}^{\mathrm{T}}\begin{bmatrix}\bar{\boldsymbol{\xi}}^*\\ \bar{\boldsymbol{\nu}}^*\end{bmatrix}\\ &= \bar{\mathbf{f}}(\bar{\mathbf{x}}^*(t),\mathbf{0}_{n_u})^{\mathrm{T}}\left(\bar{\boldsymbol{\lambda}}^*_{\bar{\phi}}(t) + \begin{bmatrix}\bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\omega}}}(t) & \bar{\boldsymbol{\lambda}}^*_{\bar{\psi}}(t)\end{bmatrix}\begin{bmatrix}\bar{\boldsymbol{\xi}}^*\\ \bar{\boldsymbol{\nu}}^*\end{bmatrix}\right) + \frac{\partial \bar{\phi}}{\partial t}\big(\bar{\mathbf{x}}^*(t_f^*),t_f^*\big)^{\mathrm{T}}\\ &\quad + \begin{bmatrix}\frac{\partial \bar{\boldsymbol{\omega}}}{\partial t}\big(\bar{\mathbf{x}}^*(t_f^*),t_f^*\big)\\ \frac{\partial \bar{\psi}}{\partial t}\big(\bar{\mathbf{x}}^*(t_f^*),t_f^*\big)\end{bmatrix}^{\mathrm{T}}\begin{bmatrix}\bar{\boldsymbol{\xi}}^*\\ \bar{\boldsymbol{\nu}}^*\end{bmatrix}\\ &= \bar{\mathbf{f}}(\bar{\mathbf{x}}^*(t),\mathbf{0}_{n_u})^{\mathrm{T}}\bar{\boldsymbol{\lambda}}^*_{\bar{\phi}}(t) + \frac{\partial \bar{\phi}}{\partial t}\big(\bar{\mathbf{x}}^*(t_f^*),t_f^*\big)^{\mathrm{T}}\\ &\quad + \left(\bar{\mathbf{f}}(\bar{\mathbf{x}}^*(t),\mathbf{0}_{n_u})^{\mathrm{T}}\begin{bmatrix}\bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\omega}}}(t) & \bar{\boldsymbol{\lambda}}^*_{\bar{\psi}}(t)\end{bmatrix} + \begin{bmatrix}\frac{\partial \bar{\boldsymbol{\omega}}}{\partial t}\big(\bar{\mathbf{x}}^*(t_f^*),t_f^*\big)^{\mathrm{T}} & \frac{\partial \bar{\psi}}{\partial t}\big(\bar{\mathbf{x}}^*(t_f^*),t_f^*\big)^{\mathrm{T}}\end{bmatrix}\right)\begin{bmatrix}\bar{\boldsymbol{\xi}}^*\\ \bar{\boldsymbol{\nu}}^*\end{bmatrix},\end{aligned} \tag{G.48}$$

implies that, if the states, inputs and adjoint variables that were computed for the solution are available for N time instants $t_1,\ldots,t_N$, the linear system of equations

$$\mathbf{0}_N = \boldsymbol{\Phi}^* + \begin{bmatrix}\boldsymbol{\Omega}^* & \boldsymbol{\Psi}^*\end{bmatrix}\begin{bmatrix}\bar{\boldsymbol{\xi}}^*\\ \bar{\boldsymbol{\nu}}^*\end{bmatrix} \tag{G.49}$$

must be satisfied, with

$$\boldsymbol{\Phi}^* = \begin{bmatrix} \bar{\mathbf{f}}(\bar{\mathbf{x}}^*(t_1), \mathbf{0}_{n_u})^{\mathrm{T}} \bar{\boldsymbol{\lambda}}^*_{\bar{\phi}}(t_1) + \frac{\partial \bar{\phi}}{\partial t}\left(\bar{\mathbf{x}}^*(t_f^*), t_f^*\right)^{\mathrm{T}} \\ \vdots \\ \bar{\mathbf{f}}(\bar{\mathbf{x}}^*(t_N), \mathbf{0}_{n_u})^{\mathrm{T}} \bar{\boldsymbol{\lambda}}^*_{\bar{\phi}}(t_N) + \frac{\partial \bar{\phi}}{\partial t}\left(\bar{\mathbf{x}}^*(t_f^*), t_f^*\right)^{\mathrm{T}} \end{bmatrix}, \tag{G.50}$$

$$\boldsymbol{\Omega}^* = \begin{bmatrix} \bar{\mathbf{f}}(\bar{\mathbf{x}}^*(t_1), \mathbf{0}_{n_u})^{\mathrm{T}} \bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\omega}}}(t_1) + \frac{\partial \bar{\boldsymbol{\omega}}}{\partial t}\left(\bar{\mathbf{x}}^*(t_f^*), t_f^*\right)^{\mathrm{T}} \\ \vdots \\ \bar{\mathbf{f}}(\bar{\mathbf{x}}^*(t_N), \mathbf{0}_{n_u})^{\mathrm{T}} \bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\omega}}}(t_N) + \frac{\partial \bar{\boldsymbol{\omega}}}{\partial t}\left(\bar{\mathbf{x}}^*(t_f^*), t_f^*\right)^{\mathrm{T}} \end{bmatrix}, \tag{G.51}$$

$$\boldsymbol{\Psi}^* = \begin{bmatrix} \bar{\mathbf{f}}(\bar{\mathbf{x}}^*(t_1), \mathbf{0}_{n_u})^{\mathrm{T}} \bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\psi}}}(t_1) + \frac{\partial \bar{\boldsymbol{\psi}}}{\partial t}\left(\bar{\mathbf{x}}^*(t_f^*), t_f^*\right)^{\mathrm{T}} \\ \vdots \\ \bar{\mathbf{f}}(\bar{\mathbf{x}}^*(t_N), \mathbf{0}_{n_u})^{\mathrm{T}} \bar{\boldsymbol{\lambda}}^*_{\bar{\boldsymbol{\psi}}}(t_N) + \frac{\partial \bar{\boldsymbol{\psi}}}{\partial t}\left(\bar{\mathbf{x}}^*(t_f^*), t_f^*\right)^{\mathrm{T}} \end{bmatrix}. \tag{G.52}$$

Then, one needs to confirm if the conditions in Eqs. (G.23) and (G.24) are satisfied for the Lagrange multipliers $\bar{\boldsymbol{\nu}}^*$.

Finally, for each instant $t \in \left[t_0, t_f^*\right]$, one can obtain the Lagrange multipliers $\bar{\boldsymbol{\mu}}^*(t)$ and $\bar{\boldsymbol{\eta}}^*(t)$ by solving the linear system of equations in Eq. (G.26) for $\bar{\boldsymbol{\mu}}^*(t)$ and $\bar{\boldsymbol{\eta}}^*(t)$ subject to the conditions in Eqs. (G.29) and (G.34). Then, one needs to confirm if the conditions in Eqs. (G.17), (G.28), (G.32) and (G.33) are satisfied.

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[168] D. Rodrigues, S. Srinivasan, N. Bhatt, J. Billeter, M. Amrhein, and D. Bonvin. Incremental model identification of reaction systems. Universidade de Santiago de Compostela, Santiago de Compostela, Spain, 2017.

Curriculum vitae

Personal information

Full name	Diogo Filipe Mateus Rodrigues
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Nationality	Portuguese
Date of birth	January 29th, 1988
Google Scholar	https://scholar.google.ch/citations?user=Deo1k24AAAAJ
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Scopus	https://www.scopus.com/authid/detail.uri?authorId=56533272200

Education

Ecole Polytechnique Fédérale de Lausanne — From December 2013 until June 2018
PhD in Chemistry and Chemical Engineering
Thesis advisor: Prof. Dominique Bonvin
Thesis: *Concept of Variants and Invariants for Reaction Systems, with Application to Estimation, Control and Optimization*

Instituto Superior Técnico - University of Lisbon — From September 2008 until September 2012
BSc and MSc in Biological Engineering
Final average grade of 19 at MSc level (20-point grading scale)
Final average grade of 18 at BSc level (20-point grading scale)
Thesis: *Production of Recombinant Human Aldehyde Oxidase in E. coli and Optimization of its Application for Preparative Synthesis of Oxidized Drug Metabolites*

Instituto Superior Técnico - University of Lisbon — From September 2005 until August 2008
BSc in Information Systems and Computer Engineering
Final average grade of 19 (20-point grading scale)

Employment history

EPF Lausanne (Lausanne, Switzerland) Doctoral Assistant Main activities: conduct and publish own research about variants and invariants for reaction systems and their applications, under supervision of Prof. Dominique Bonvin, and be responsible for teaching activities and supervision of undergraduate students	From December 2013 until June 2018
Novartis Pharma AG (Basel, Switzerland) Scientific Associate (temporary) Main activities: screen the derivatives of research compounds formed by enzyme preparations, and produce and purify these derivatives on a preparative scale	From April 2013 until November 2013
Novartis Pharma AG (Basel, Switzerland) Trainee in Continuous Manufacturing Main activities: plan, perform, and document experiments to develop and optimize the production of monoclonal antibodies through animal cell culture in perfusion bioreactors	From October 2012 until March 2013
Novartis Pharma AG (Basel, Switzerland) Master Student Main activities: plan, perform, and document experiments to optimize the activity of a recombinant human enzyme	From March 2012 until August 2012

Publications in peer-reviewed scientific journals

- D. Rodrigues, J. Billeter, and D. Bonvin. Maximum-likelihood estimation of kinetic parameters via the extent-based incremental approach. *Comput. Chem. Eng.*, in press, 2018.

Link: http://doi.org/10.1016/j.compchemeng.2018.05.024

- D. Rodrigues, M. Amrhein, J. Billeter, and D. Bonvin. Fast estimation of plant steady state for imperfectly known dynamic systems, with application to real-time optimization. *Ind. Eng. Chem. Res.*, 57(10):3699–3716, 2018.

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- J. Billeter, D. Rodrigues, S. Srinivasan, M. Amrhein, and D. Bonvin. On decoupling rate processes in chemical reaction systems – methods and applications. *Comput. Chem. Eng.*, 114:296–305, 2018.

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- D. Rodrigues, J. Billeter, and D. Bonvin. Semi-analytical solutions for tubular chemical reactors. *Chem. Eng. Sci.*, 172:239–249, 2017.

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- D. Rodrigues, J. Billeter, and D. Bonvin. Generalization of the concept of extents to

distributed reaction systems. *Chem. Eng. Sci.*, 171:558–575, 2017.

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- D. Bonvin, C. Georgakis, C. C. Pantelides, M. Barolo, M. A. Grover, D. Rodrigues, R. Schneider, and D. Dochain. Linking models and experiments. *Ind. Eng. Chem. Res.*, 55(25):6891–6903, 2016.

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- D. Rodrigues, S. Srinivasan, J. Billeter, and D. Bonvin. Variant and invariant states for chemical reaction systems. *Comput. Chem. Eng.*, 73:23–33, 2015.

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- D. Rodrigues, M. Kittelmann, F. Eggimann, T. Bachler, S. Abad, A. Camattari, A. Glieder, M. Winkler, and S. Lütz. Production of recombinant human aldehyde oxidase in Escherichia coli and optimization of its application for the preparative synthesis of oxidized drug metabolites. *ChemCatChem*, 6(4):1028–1042, 2014.

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Publications in peer-reviewed conference proceedings

- D. Rodrigues and D. Bonvin. Parsimonious input parameterization for dynamic optimization problems. *Comput. Aided Chem. Eng.*, 44:769–774, 2018.

Link: http://doi.org/10.1016/B978-0-444-64241-7.50123-3

- D. Bonvin, S. Srinivasan, D. Rodrigues, J. Billeter, and M. Amrhein. Concept and applications of extents in chemical reaction systems. In *FOCAPO-CPC*, Tucson, AZ, 2017.

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- D. Rodrigues, J. Billeter, and D. Bonvin. Global identification of kinetic parameters via the extent-based incremental approach. *Comput. Aided Chem. Eng.*, 40:2119–2124, 2017.

Link: http://doi.org/10.1016/B978-0-444-63965-3.50355-X

- D. Rodrigues, J. Billeter, and D. Bonvin. Incremental model identification of distributed two-phase reaction systems. *IFAC-PapersOnLine*, 48(8):266–271, 2015.

Link: http://doi.org/10.1016/j.ifacol.2015.08.192

- D. Rodrigues, J. Billeter, and D. Bonvin. Control of reaction systems via rate estimation and feedback linearization. *Comput. Aided Chem. Eng.*, 37:137–142, 2015.

Link: http://doi.org/10.1016/B978-0-444-63578-5.50018-9

Contributions to international conferences

Peer-reviewed conference abstracts

- D. Rodrigues, J. Billeter, and D. Bonvin. Optimal control laws for batch and semi-batch reactors using the concept of extents. In *AIChE Annual Meeting*, Minneapolis, MN, 2017.

Link: https://aiche.confex.com/aiche/2017/meetingapp.cgi/Paper/494521

- A. Oulevey, D. Rodrigues, J. Billeter, and D. Bonvin. Generalized incremental model identification for chemical reaction systems. In *SCS Fall Meeting 2017*, Bern, Switzerland, 2017.

Link: http://fm17.chemistrycongresses.ch/abstracts/search-abstracts/abstractform/458?layout=preview&tmpl=component

- D. Rodrigues, M. Amrhein, J. Billeter, and D. Bonvin. Fast estimation of plant steady state, with application to static RTO. In *AIChE Annual Meeting*, San Francisco, CA, 2016.

Link: https://aiche.confex.com/aiche/2016/webprogram/Paper455266.html

- V. Chhabra, D. Rodrigues, S. Srinivasan, J. Billeter, and D. Bonvin. Extent-based model identification of surface catalytic reaction systems. In *SCS Fall Meeting 2014*, Zurich, Switzerland, 2014.

Link: http://chemistrycongresses.ch/index.php?option=com_scs&layout=preview&from=all&id=622&tmpl=component

Oral presentations

- D. Rodrigues and D. Bonvin. Parsimonious input parameterization for dynamic optimization problems. *Comput. Aided Chem. Eng.*, 44:769–774, 2018.

Link: http://doi.org/10.1016/B978-0-444-64241-7.50123-3

- D. Rodrigues, J. Billeter, and D. Bonvin. Optimal control laws for batch and semi-batch reactors using the concept of extents. In *AIChE Annual Meeting*, Minneapolis, MN, 2017.

Link: https://aiche.confex.com/aiche/2017/meetingapp.cgi/Paper/494521

- D. Rodrigues, J. Billeter, and D. Bonvin. Global identification of kinetic parameters via the extent-based incremental approach. *Comput. Aided Chem. Eng.*, 40:2119–2124, 2017.

Link: http://doi.org/10.1016/B978-0-444-63965-3.50355-X

- D. Rodrigues, M. Amrhein, J. Billeter, and D. Bonvin. Fast estimation of plant steady state, with application to static RTO. In *AIChE Annual Meeting*, San Francisco, CA, 2016.

Link: https://aiche.confex.com/aiche/2016/webprogram/Paper455266.html

- D. Rodrigues, J. Billeter, and D. Bonvin. Control of reaction systems via rate estimation and feedback linearization. *Comput. Aided Chem. Eng.*, 37:137–142, 2015.

Link: http://doi.org/10.1016/B978-0-444-63578-5.50018-9

Poster presentations

- A. Oulevey, D. Rodrigues, J. Billeter, and D. Bonvin. Generalized incremental model identification for chemical reaction systems. In *SCS Fall Meeting 2017*, Bern, Switzerland, 2017.

Link: http://fm17.chemistrycongresses.ch/abstracts/search-abstracts/abstractform/458?layout=preview&tmpl=component

- V. Chhabra, D. Rodrigues, S. Srinivasan, J. Billeter, and D. Bonvin. Extent-based model identification of surface catalytic reaction systems. In *SCS Fall Meeting 2014*, Zurich, Switzerland, 2014.

Link: http://chemistrycongresses.ch/index.php?option=com_scs&layout=preview&from=all&id=622&tmpl=component

Outreach activities

Invited seminars in other universities

- D. Rodrigues, S. Srinivasan, N. Bhatt, J. Billeter, M. Amrhein, and D. Bonvin. Incremental model identification of reaction systems. KTH Royal Institute of Technology, Stockholm, Sweden, 2018.

Link: https://www.kth.se/ac/calendar/seminars/incremental-model-identification-of-reaction-systems-1.796542

- D. Rodrigues, S. Srinivasan, N. Bhatt, J. Billeter, M. Amrhein, and D. Bonvin. Incremental model identification of reaction systems. Universidade de Santiago de Compostela, Santiago de Compostela, Spain, 2017.

Link: http://www.itmati.com/en/node/27136

Institutional responsibilities

• Treasurer and member of the Board of the local group of the Board of European Students of Technology in Lisbon (from June 2011 until May 2012)

Supervision of students

Adrien Oulevey (master project)	Spring 2016/2017
Abeynaya Gnanasekaran (internship)	Summer 2015
Matteo Keller (master project)	Spring 2014/2015
Vibhuti Chhabra (master project)	Spring 2013/2014

Teaching activities

Control Systems (hands-on laboratory sessions)	Fall - From 2014/2015 until 2017/2018
Process Control (problem sessions)	Spring - From 2014/2015 until 2016/2017
Dynamical Systems (problem sessions)	Spring - From 2015/2016 until 2016/2017

Active memberships in scientific societies

• Member number 9901790216 of AIChE (American Institute of Chemical Engineers) since 2016

Prizes and awards

• "Best Students of UTL/Santander Totta Award" for the best final year students of the former Technical University of Lisbon (UTL) in 2012
• Awarded with merit scholarship by UTL for outstanding academic performance (best student in the degree) in 2007, 2008, 2010 and 2011

Personal skills

Language skills

Portuguese	Mother tongue
English	CEFR level C2 - proficient user
	Certificate in Advanced English, Grade A - December 2010
French	CEFR level B2 - independent user
	Certificate from the EPFL Language Center - January 2016

Technical skills and competences

• Typesetting (LaTeX) and programming (C, MATLAB, Mathematica) tools and languages
• Experience with Windows, Mac OS, Linux, Office, Adobe Reader, Adobe Illustrator, LabVIEW
• Operation of diverse lab equipment (microscopes, filters, columns, reactors, spectrometers, etc)