

Vessel Extents for Chemical Reaction Systems – Concepts and Applications

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- Generic models of reaction systems
- Modeling issues
 - Minimal dimensionality, redundant states, invariant relationships
 - Decoupled states, individual extents
 - Concept of **vessel extents**
- Application areas
 - A1. Data reconciliation
 - A2. Rate estimation
 - A3. Kinetic identification
 - A4. State reconstruction
 - A5. State estimation
 - A6. Others
- Conclusions

Models of chemical reaction systems

- A large variety of reactions
 - Liquid-phase, gas-phase, surface
 - Catalytic, inhibition
 - Fast, slow, equilibrium, etc.
- A large variety of reactors
 - Lumped vs. distributed
 - Continuous vs. discontinuous (batch, semi-batch)
 - Homogeneous vs. heterogeneous (multiphase)
 - Isothermal vs. non-isothermal, etc.
- Common model elements
 - **Balance equations**: state variables $\mathbf{c}(t)$, $\mathbf{p}(t)$, $T(t)$
(partial) differential equations, additive rate terms → **exploit** structure
 - **Rate processes**: for reactions, mass transfers, heat transfers
algebraic relationships, often poorly known → **investigate** rates

- Minimal dimensionality
 - Redundant states?
 - Invariant relationships?
 - Are these relationships reaction system dependent?
- Decoupled states
 - Is it possible to decouple the rate processes?
 - Properties of decoupled states?
- Answer: state transformation
 - From concentrations and temperatures to decoupled extents
 - Systematic generation of invariant relationships

Homogeneous reaction systems

Balance equations

Nonisothermal homogeneous reaction system consisting of S species, R independent reactions, p inlet streams, and 1 outlet stream

Mole balances for S species

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

$$(S) \quad (S \times R) \quad (R) \quad (S \times p) \quad (p) \quad \mathbf{r}_v(t) := V(t) \mathbf{r}(t), \quad \omega(t) := \frac{u_{out}(t)}{m(t)}$$

Mass m , volume V and molar concentrations \mathbf{c}

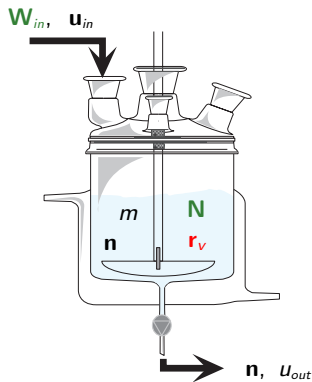
$$m(t) = \mathbf{1}_S^T \mathbf{M}_w \mathbf{n}(t), \quad V(t) = \frac{m(t)}{\rho(t)}, \quad \mathbf{c}(t) = \frac{\mathbf{n}(t)}{V(t)}$$

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

Global macroscopic view

Valid regardless of temperature, catalyst, solvent

Redundant information $m(t)$



Homogeneous reaction systems

Objective: Decoupled reaction system in terms of vessel extents

- S-dimensional model equations

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

- Decoupled reaction model in terms of vessel extents

$$\begin{aligned} \dot{x}_{r,i}(t) &= r_{v,i}(t) - \omega(t) x_{r,i}(t) & x_{r,i}(0) &= 0 & i &= 1, \dots, R \\ \dot{x}_{in,j}(t) &= u_{in,j}(t) - \omega(t) x_{in,j}(t) & x_{in,j}(0) &= 0 & j &= 1, \dots, p \\ \dot{x}_{ic}(t) &= -\omega(t) x_{ic}(t) & x_{ic}(0) &= 1 & & \end{aligned}$$

- **Vessel extents** are extents discounted by the amount of material that has left the reactor
- $(R + p + 1)$ -dimensional system
- Very useful although only apparent decoupling as $r_{v,i}(t)$ is an **endogenous input** and not an independent input!

Homogeneous reaction systems

Procedure: Four-way decomposition into extents and invariants ¹

- Model with zero initial conditions

$$\dot{\mathbf{n}}(t) = \mathbf{N}^T \mathbf{r}_v(t) + \mathbf{W}_{in} \mathbf{u}_{in}(t) + \mathbf{n}_0 \delta(t) - \omega(t) \mathbf{n}(t), \quad \mathbf{n}(0) = \mathbf{0}_S$$

- Assumption: $\text{rank}([\mathbf{N}^T \mathbf{W}_{in} \mathbf{n}_0]) = R + p + 1$. Linear transformation

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \\ \mathbf{x}_{iv}(t) \end{bmatrix} = \mathcal{T} \mathbf{n}(t) \quad \mathcal{T} = [\mathbf{N}^T \mathbf{W}_{in} \mathbf{n}_0 \mathbf{P}]^{-1}$$

- Vessel extents of reaction \mathbf{x}_r , inlet \mathbf{x}_{in} , initial conditions x_{ic} , and invariants \mathbf{x}_{iv}

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \omega(t) \mathbf{x}_r(t) \quad \mathbf{x}_r(0) = \mathbf{0}_R$$

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) - \omega(t) \mathbf{x}_{in}(t) \quad \mathbf{x}_{in}(0) = \mathbf{0}_p$$

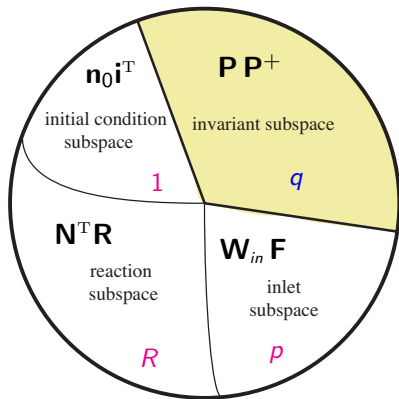
$$\dot{x}_{ic}(t) = -\omega(t) x_{ic}(t) \quad x_{ic}(0) = 1$$

$$\mathbf{x}_{iv}(t) = \mathbf{0}_q$$

¹ D. Rodrigues et al., *Comput. Chem. Engng*, 73, 23-33 (2015).

Homogeneous reaction systems

Four subspaces, transformation possible if $S \geq d$



S-dimensional space of species

$R + p + 1$ variants

$q = S - R - p - 1$ invariants

$$\mathcal{T} = \begin{bmatrix} \mathbf{R} \\ \mathbf{F} \\ \mathbf{i}^T \\ \mathbf{P}^+ \end{bmatrix} = [\mathbf{N}^T \ \mathbf{W}_{in} \ \mathbf{n}_0 \ \mathbf{P}]^{-1}$$

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \\ \mathbf{x}_{iv}(t) \end{bmatrix} = \mathcal{T} \mathbf{n}(t)$$

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

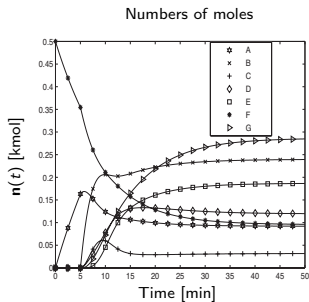
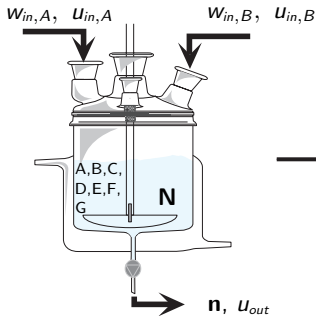
$$\mathbf{x}_{iv}(t) = \mathbf{P}^+ \mathbf{n}(t) = \mathbf{0}_q$$

Homogeneous reaction systems

Example 1: Ethanolysis reaction in an homogeneous CSTR

- Seven species ($S = 7$), three reactions ($R = 3$), two inlets ($p = 2$) and one outlet
- Stoichiometric matrix \mathbf{N} , inlet-composition matrix \mathbf{W}_{in} and initial conditions \mathbf{n}_0 :

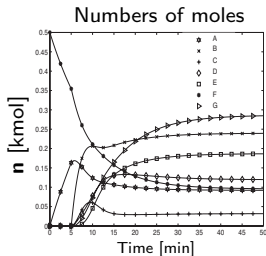
$$\mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 1 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 & 0 & 0 \\ 0 & -1 & 0 & -1 & 0 & 1 & 1 \end{bmatrix} \quad \mathbf{W}_{in} = \begin{bmatrix} w_{in,A} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & w_{in,B} & 0 & 0 & 0 & 0 & 0 \end{bmatrix}^T \quad \mathbf{n}_0$$



Reaction extents?

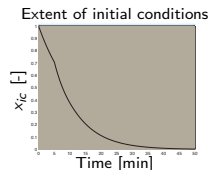
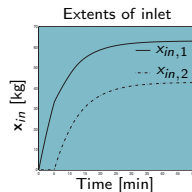
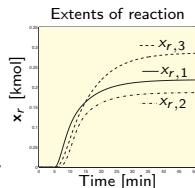
Homogeneous reaction systems

Computation of extents



$$\mathcal{J} = \begin{bmatrix} R \\ F \\ \mathbf{i}^T \\ P^+ \end{bmatrix}$$

N W_{in} n_0



One invariant $x_{iv}(t) = P^+ \mathbf{n}(t) = 0$

x

y

\mathcal{J}

Generalization to other reaction systems

- Homogeneous reaction systems with heat balance²
 - Additional heat balance equation
 - Additional decoupled extent of heat exchange
- Gas-liquid reaction systems³
 - Balance equation for both the gas and liquid phases
 - Additional decoupled extents of mass transfer
- Distributed reaction systems⁴
 - One- and two-dimensional tubular reactors, reactive distillation and absorption columns
 - Additional decoupled extents of diffusion and mass transfer

² D. Rodrigues *et al.*, *Comput. Chem. Engng*, 73, 23-33 (2015).

³ N. Bhatt *et al.*, *Ind. Eng. Chem. Res.*, 49, 7704-7717 (2010).

⁴ D. Rodrigues *et al.*, *Chem. Eng. Sci.* (submitted).

- Models of chemical reaction systems
 - Generic elements
- Modeling issues
 - True dimensionality, redundant states, invariant relationships
 - Decoupled states, individual extents
 - Concept of **vessel extents**, generalization to several reactor types
- Application areas
 - A1. Data reconciliation
 - A2. Rate estimation
 - A3. Kinetic identification
 - A4. State reconstruction
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- Conclusions

A1. Data reconciliation ⁵

- Constraints valid at current time instant

- q invariant relationships that exploit redundancies in balance equations:

$$\mathbf{P}^+ \mathbf{n}(t) = \mathbf{0}_q$$

- Positivity, $\mathbf{n}(t) \geq \mathbf{0}_s$

- Shape constraints valid over time

- Monotonicity
- Convexity/concavity

- Sources of shape constraints

- **Prior knowledge**, from reaction scheme and reactor operation
- **Prior measurements**, if necessary via differentiation

⁵ S. Srinivasan et al., *Comput. Chem. Engng* (submitted).

Data reconciliation

In terms of extents

- Use shape constraints as algebraic constraints

$$\hat{\mathbf{x}}(t_{1:H}) = \arg \min_{\mathbf{x}(t_{1:H})} \sum_{h=1}^H (\tilde{\mathbf{n}}(t_h) - \mathbf{n}(t_h))^T \mathbf{W}(t_h) (\tilde{\mathbf{n}}(t_h) - \mathbf{n}(t_h))$$

s.t. $\mathbf{n}(t_{1:H}) = [\mathbf{N}^T \mathbf{W}_m \mathbf{n}_0] \mathbf{x}(t_{1:H})$ (Reconstruction)

$\mathbf{n}(t_{1:H}) \geq \mathbf{0}_{S \times H}$ (Positivity constraints on \mathbf{n})

$\mathbf{x}(t_{1:H}) \geq \mathbf{0}_{d \times H}$ (Positivity constraints on \mathbf{x})

$\mathcal{K}_x(\mathbf{x}(t_{1:H})) \leq \mathbf{0}_{k_x \times H}$ (Knowledge-based constraints on \mathbf{x})

$\mathcal{M}_x(\mathbf{x}(t_{1:H})) \leq \mathbf{0}_{m_x \times H}$ (Measurement-based constraints on \mathbf{x})

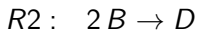
Data reconciliation

Example 2: Acetoacetylation of pyrrole

- CSTR with $S = 7$, $R = 4$, $p = 1$, and one outlet



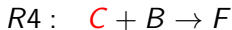
$$r_1 = k_1 C_A C_B C_K$$



$$r_2 = k_2 C_B^2 C_K$$



$$r_3 = k_3 C_B$$



$$r_4 = k_4 C_C C_B C_K$$

- The reaction system has two invariant relationships:

$$n_K(t) - 0.05 n_A(t) - 0.08 n_B(t) - 0.13 n_C(t) - 0.16 n_D(t) - 0.08 n_E(t) - 0.21 n_F(t) = 0$$

$$\mathbf{1}_S^T \mathbf{M}_w \mathbf{n}_0 - \mathbf{1}_S^T \mathbf{M}_w \mathbf{n}(t) = 0$$

Data reconciliation

Shape constraints

Table: Measurement-based constraints for species and constraints. (\smile) denotes convex shape and (\frown) denotes concave shape.

Species	Monotonicity	Until	Shape	Until
A	–	15.0 min	\smile	15.0 min
B	–	16.5 min	\smile	14.5 min
C	+	22.0 min	\frown	22.0 min
D	+	13.5 min	\frown	13.5 min
E	+	23.0 min	\frown	30.0 min
F	+	27.0 min	\frown	30.0 min
K	none	–	none	–
$x_{r,1}$	+	30.0 min	\frown	30.0 min
$x_{r,2}$	+	30.0 min	\frown	30.0 min
$x_{r,3}$	+	30.0 min	\frown	30.0 min
$x_{r,4}$	+	30.0 min	\frown	30.0 min

Data reconciliation

Start up of CSTR

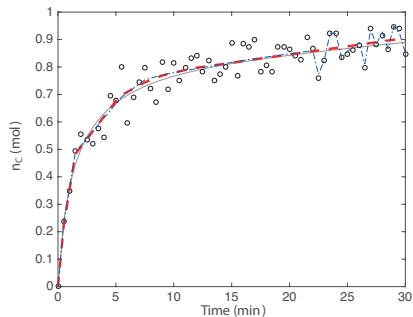
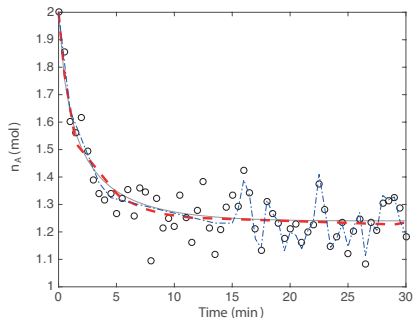


Figure: Numbers of moles of species A and C: True (—), measured (o) and reconciled via \mathbf{n} (-.-) and \mathbf{x} (- -).

A2. Rate estimation ⁶

Without kinetic model, via numerical differentiation of measured concentrations

- Online computation of reaction rates $\hat{\mathbf{r}}_v(t)$
 - Computation of $\tilde{\mathbf{x}}_r(t) = \mathbf{R} \tilde{\mathbf{n}}(t)$
 - **Reconciliation** of $\tilde{\mathbf{x}}_r(t)$ to obtain $\hat{\mathbf{x}}_r(t)$
 - Numerical differentiation of $\hat{\mathbf{x}}_r(t)$ via e.g. first-order differentiation Savitzky-Golay filter ⁷
 - Computation of $\hat{\mathbf{r}}_v(t) = \dot{\hat{\mathbf{x}}}_r(t) + \tilde{\omega}(t) \hat{\mathbf{x}}_r(t)$
- Application of estimated rates
 - To implement feedback linearization and **online control** ⁸
 - To speed up estimation of steady state of slow states in **static RTO** ⁹

⁶ S. Srinivasan *et al.*, *IFAC Dycops*, Trondheim (2016).

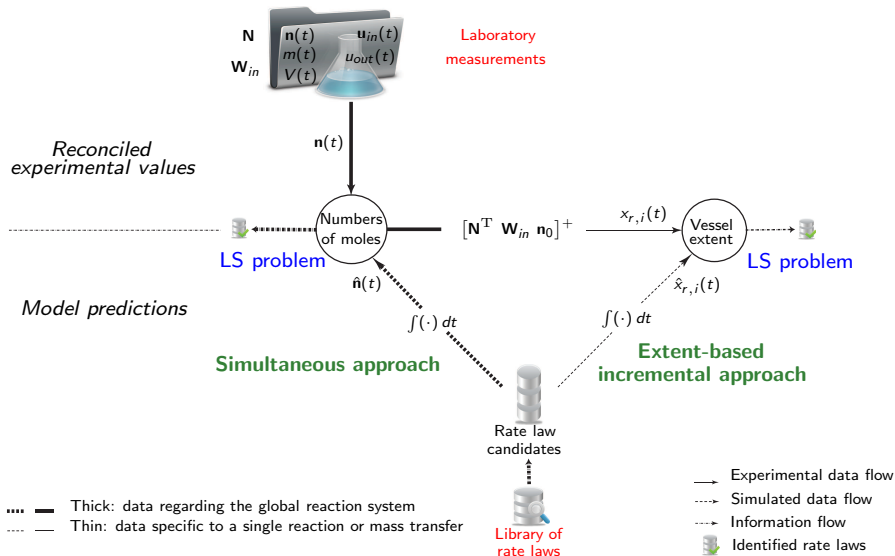
⁷ A. Savitzky and M. J. E. Golay, *Anal. Chem.*, 36, 1627-1639 (1964).

⁸ D. Rodrigues *et al.*, *PSE 2015/Escape-25*, Copenhagen, Denmark (2015).

⁹ D. Rodrigues *et al.*, *AIChE Annual Meeting*, San Francisco, CA (2016).

A3. Kinetic identification

Simultaneous and incremental approaches ¹⁰



¹⁰ N. Bhatt *et al.*, *Ind. Eng. Chem. Res.*, 50, 12960-12974 (2011).

Incremental kinetic identification

Example 3: Chlorination of Butanoic Acid (gas-liquid reaction system)

- Identification of rate expression for the main reaction R1
- Rate expression candidates

Reaction R1

$$r_1^{(1)} = k_1 c_{BA} c_{Cl_2}$$

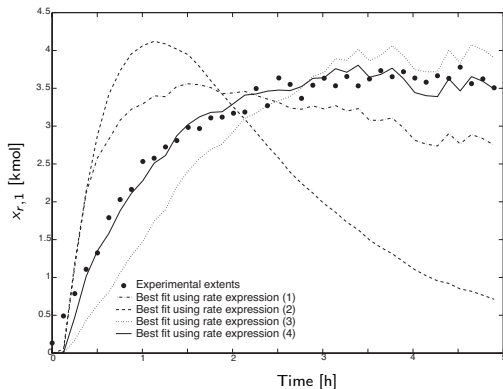
$$r_1^{(2)} = k_1 c_{Cl_2}$$

$$r_1^{(3)} = k_1 c_{BA} c_{Cl_2} c_{MBA}$$

$$r_1^{(4)} = k_1 c_{BA} c_{Cl_2} \sqrt{c_{MBA}}$$

- Identified rate expression for R1

$$r_1^{(4)} = 1.3543 c_{BA} c_{Cl_2} \sqrt{c_{MBA}}$$



Incremental kinetic identification

Estimation of kinetic and mass-transfer parameters

- Identified rate expressions

Rate expressions
$r_1 = k_1 c_{BA} c_{Cl_2} \sqrt{c_{MBA}}$
$r_2 = k_2 r_1 c_{Cl_2}$
$\zeta_{gl, Cl_2} = k_{Cl_2} A_s V_l M_{w, Cl_2} (c_{Cl_2}^* - c_{Cl_2})$
$\zeta_{lg, HCl} = k_{HCl} A_s V_l M_{w, HCl} (c_{HCl} - c_{HCl}^*)$

- Results of curve fitting (with 2% measurement noise)

Parameters	True simulated values	Initial values	Estimated values	99% Confidence intervals
$k_1 [(\text{m}^3 \text{ kmol}^{-1})^{\frac{3}{2}}]$	1.3577	0.8000	1.3543	[1.3207, 1.3879]
$k_2 [\text{m}^3 \text{ kmol}^{-1}]$	0.1	0.0200	0.105	[0.0884, 0.1216]
$k_{Cl_2} [\text{m s}^{-1}]$	0.666×10^{-4}	0.0002	0.594×10^{-4}	$[0.514 \times 10^{-4}, 0.674 \times 10^{-4}]$
$k_{HCl} [\text{m s}^{-1}]$	0.845×10^{-4}	0.0002	0.813×10^{-4}	$[0.763 \times 10^{-4}, 0.863 \times 10^{-4}]$

A4. State reconstruction

Various ways

• Motivation

- Reconstruct the state $\mathbf{n}(t)$ from a limited number of measurements, $\mathbf{n}_a(t)$
- Whenever possible, **without the use of a kinetic model**

• If $S_a \geq d$, use $\mathbf{n}_a(t)$ directly

- Compute $\mathbf{x}_r(t)$, $\mathbf{x}_{in}(t)$ and $x_{ic}(t)$ via linear transformation
- Reconstruct $\mathbf{n}(t)$ from $\mathbf{x}_r(t)$, $\mathbf{x}_{in}(t)$ and $x_{ic}(t)$

• If $S_a \geq R$, use $\mathbf{u}_{in}(t)$, $u_{out}(t)$, and $\mathbf{n}_a(t)$

- Compute $\mathbf{x}_{in}(t)$ and $x_{ic}(t)$ via numerical integration of $\mathbf{u}_{in}(t)$ and $u_{out}(t)$
- Compute $\mathbf{x}_r(t)$ via linear transformation

• If $S_a < R$, use a kinetic model

State estimation ¹¹

Use a kinetic model

- Knowledge of
 - stoichiometry \mathbf{N} , inlet concentrations \mathbf{W}_{in} and initial conditions \mathbf{n}_0
 - kinetic model $\mathbf{r}(\mathbf{c}, \boldsymbol{\theta})$
 - $\mathbf{u}_{in}(\tau)$, $\omega(\tau)$, $V(\tau)$ and measured outputs $\mathbf{y}(\tau)$, $0 \leq \tau \leq t$
- Estimate the state vector $\mathbf{n}(t)$ or $\mathbf{x}(t)$
 - Prediction step of EKF
 - Update step of RNK (receding-horizon nonlinear Kalman filter) formulated as an optimization problem, with incorporation of **shape constraints**

¹¹ S. Srinivasan *et al.*, *IFAC Dycops*, Trondheim (2016).

State estimation

Example 4: Semi-batch reactor

- Consider the following reaction system in a semi-batch reactor:



- Species B is fed to the reactor with the mass flowrate 5 g min^{-1}
- The concentration of C is measured (5% measurement noise)
- The RNK estimator uses the correct model structure but incorrect parameter values, $\bar{k}_1 = 0.75$ and $\bar{k}_2 = 0.5$
- The measurement and process noise matrices are assumed to be known

State estimation

Estimated numbers of moles

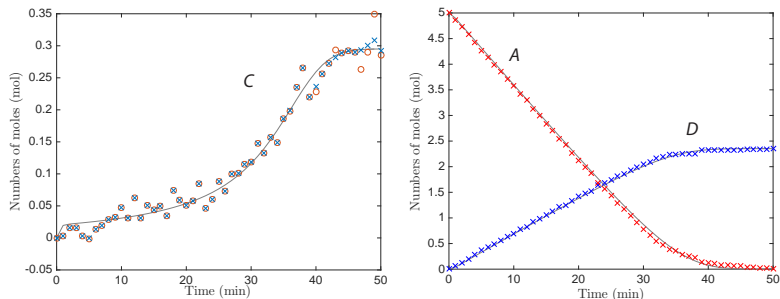


Figure: True (—), measured (\circ) and estimated (\times) numbers of moles for species A, C and D

Table: RMSE for the estimated numbers of moles.

Species	Unconstrained	Knowledge-based (\mathcal{K}) constraints	
	EKF via \mathbf{n}	via \mathbf{n}	via \mathbf{x}
A	0.375	0.283	0.052
B	0.115	0.055	0.027
C	0.016	0.014	0.013
D	0.486	0.140	0.027

- Linear transformation of the numbers of moles to extents
 - Decoupled states for reactions, mass and heat transfers
 - Invariant states that can be discarded → model reduction
 - Invariant relationships that can be used to reconcile noisy data
- Useful for the investigation of reaction systems with respect to
 - Data reconciliation, kinetic identification, state estimation
 - Model reduction via singular perturbation
 - Control using rate estimation
 - Static RTO via rate estimation
- Applicable to
 - Most reaction systems and reactor types
 - In principle, systems with more balance equations than rates