ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Laboratoire d'Automatique

Incremental Model Identification of Fluid-Fluid Reaction Systems

Dynamic accumulation and reactions in the diffusion layer

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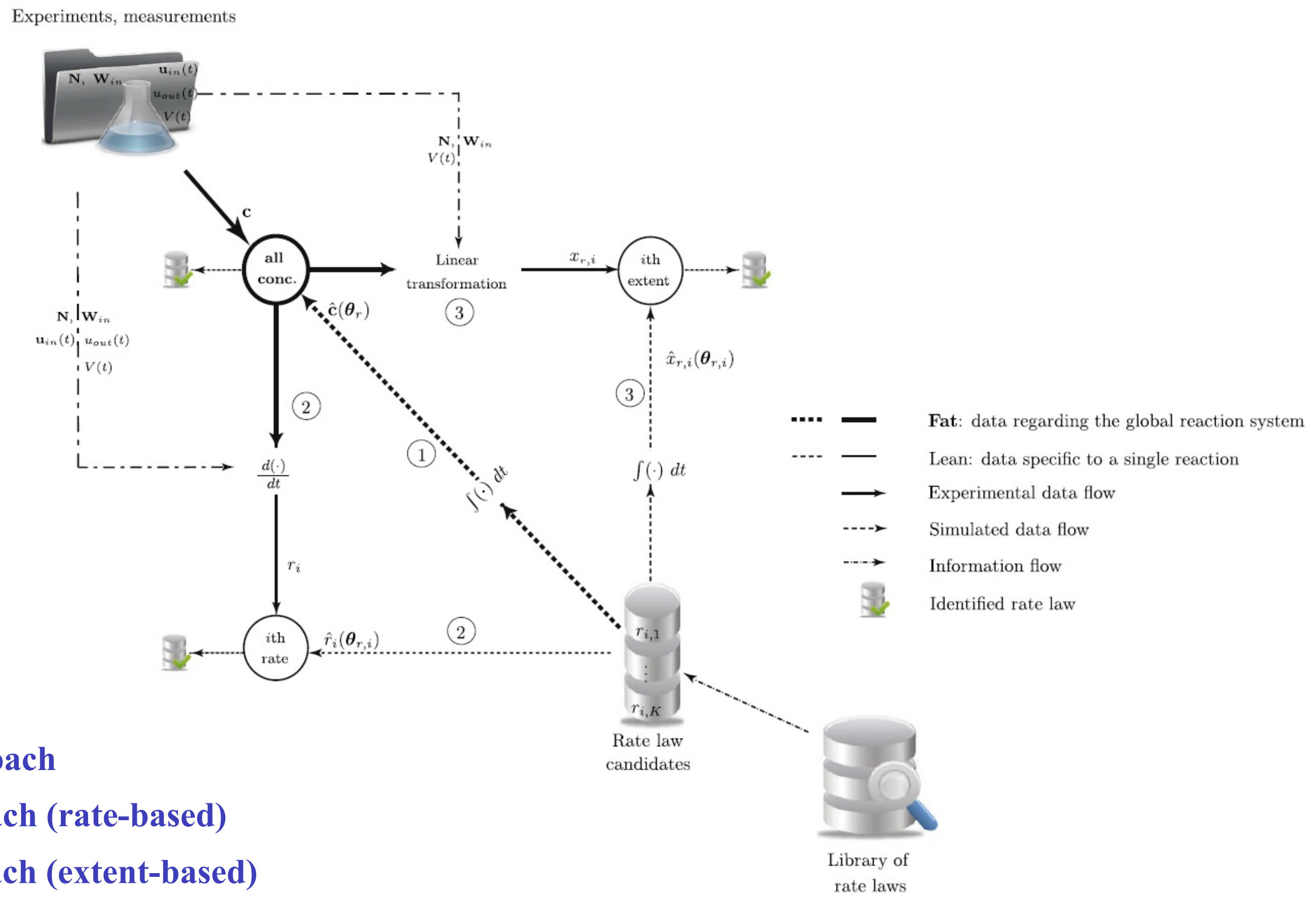
Kinetic identification

From data to rates



① **Simultaneous approach**

② **Incremental approach (rate-based)**

③ **Incremental approach (extent-based)**

Incremental model identification
Extent-based method

- The kinetic problem is decomposed into sub-problems of lower complexity that are solved individually.

- The model identification proceeds in **two steps**:
  - **Transformation to extents (v+iv)**
    Computation of the contribution of each dynamic effect (reaction, mass transfer, inlets and outlet) as *vessel extents*
  - **Model identification (Parameter estimation)**
    Individual model identification of each effect from its corresponding *vessel extent* with the integral method of parameter estimation.

Definitions
Concept of vessel extent

A 'vessel extent' indicates the quantity of material (moles, mass, volume) or energy that has been added to or withdrawn from the reactor by a given dynamic effect, and that is still in the reactor.

Differential vessel extent (i-th effect ϕ)

$$\dot{x}_{\phi,i}(t) = \xi_{\phi,i}(t) - \omega(t)x_{\phi,i}(t) \qquad x_{\phi,i}(0) = 0$$

Definitions
Vessel extents of reaction and mass transfer

- Vessel extent of the *i*-th reaction $x_{r,i}(t)$:
  number of moles produced by the *i*-th reaction still in the reactor

Differential vessel extent of reaction

$$\dot{x}_{r,i}(t) = r_{v,i}(t) - \omega(t) x_{r,i}(t) \qquad x_{r,i}(0) = 0$$

- Vessel extent of the *j*-th mass transfer $x_{m,j}(t)$:
  mass transferred by the *j*-th mass transfer that is still in the reactor

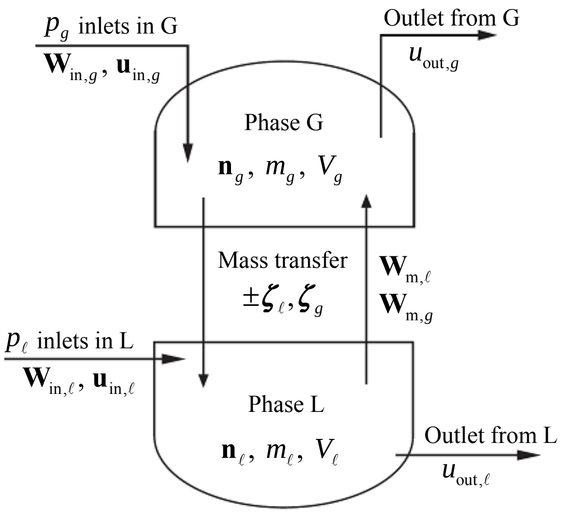
Differential vessel extent of mass transfer

$$\dot{x}_{m,j}(t) = \zeta_j(t) - \omega(t) x_{m,j}(t) \qquad x_{m,j}(0) = 0$$

Mole balance equations for the bulks of Fluid-Fluid reaction systems

Let's define Fluid-Fluid reaction systems as consisting of 2 phases B∈ {L,G} with S_b species in each phase and the following dynamic effects:

- R_b reactions
- p_m mass transfers
- p_b inlets
- 1 outlet



Mole balances on phase B

$B \in \{L,G\},\ b \in \{\ell, g\},\ \omega_b(t) = \frac{u_{out,b}(t)}{m_b(t)}$

$$\dot{\mathbf{n}}_b(t) = \mathbf{N}_b^T \mathbf{r}_{v,b}(t) \pm \mathbf{W}_{m,b} \boldsymbol{\zeta}_b(t) + \mathbf{W}_{in,b} \mathbf{u}_{in,b}(t) - \omega_b(t)\mathbf{n}_b(t), \qquad \mathbf{n}_b(0) = \mathbf{n}_{0,b}$$

S_b $\quad S_b \times R_b$ $\quad R_b$ $\quad S_b \times p_m$ $\quad p_m$ $\quad S_b \times p_b$ $\quad p_b$ $\quad S_b$

Transformation in variants and invariants

- Condition: $\mathrm{rank}([\mathbf{N}_b^{\mathrm{T}}\ \mathbf{W}_{m,b}\ \mathbf{W}_{in,b}\ \mathbf{n}_{0,b}]) = d := R_b + p_m + p_b + 1$

$$\mathbf{x}(t) = \begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_m(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \\ \mathbf{x}_{iv}(t) \end{bmatrix} := \begin{bmatrix} \mathbf{R}_b \\ \mathbf{M}_b \\ \mathbf{F}_b \\ \mathbf{q}_b^{\mathrm{T}} \\ \mathbf{Q}_b \end{bmatrix} \mathbf{n}_b(t) = \mathbf{T}\ \mathbf{n}_b(t) \qquad b \in \{\ell, g\}$$

- Vessel extents (variants) and $q_b = S_b - R_b - p_m - p_b - 1$ invariants

$$\dot{\mathbf{x}}_{r,b}(t) = \underbrace{\mathbf{R}_b\ \mathbf{N}_b^{\mathrm{T}}}_{\mathbf{I}_{R_b}} \mathbf{r}_{v,b}(t) \pm \underbrace{\mathbf{R}_b\ \mathbf{W}_{m,b}}_{\mathbf{0}} \zeta_b(t) + \underbrace{\mathbf{R}_b\ \mathbf{W}_{in,b}}_{\mathbf{0}} \mathbf{u}_{in,b}(t) - \omega_b(t)\mathbf{x}_{r,b}(t), \qquad \mathbf{x}_{r,b}(0) = \mathbf{0}_{R_b}$$

$$\dot{\mathbf{x}}_{m,b}(t) = \underbrace{\mathbf{M}_b \mathbf{N}_b^{\mathrm{T}}}_{\mathbf{0}} \mathbf{r}_{v,b}(t) \pm \underbrace{\mathbf{M}_b \mathbf{W}_{m,b}}_{\mathbf{I}_{p_m}} \zeta_b(t) + \underbrace{\mathbf{M}_b \mathbf{W}_{in,b}}_{\mathbf{0}} \mathbf{u}_{in,b}(t) - \omega_b(t)\mathbf{x}_{m,b}(t), \qquad \mathbf{x}_{m,b}(0) = \mathbf{0}_{p_m}$$

$$\dot{\mathbf{x}}_{in,b}(t) = \underbrace{\mathbf{F}_b\ \mathbf{N}_b^{\mathrm{T}}}_{\mathbf{0}} \mathbf{r}_{v,b}(t) \pm \underbrace{\mathbf{F}_b\ \mathbf{W}_{m,b}}_{\mathbf{0}} \zeta_b(t) + \underbrace{\mathbf{F}_b\ \mathbf{W}_{in}}_{\mathbf{I}_{p_b}} \mathbf{u}_{in,b}(t) - \omega_b(t)\mathbf{x}_{in,b}(t), \qquad \mathbf{x}_{in,b}(0) = \mathbf{0}_{p_b}$$

$$\dot{x}_{ic,b}(t) = \underbrace{\mathbf{q}_b^{\mathrm{T}}\ \mathbf{N}_b^{\mathrm{T}}}_{\mathbf{0}} \mathbf{r}_{v,b}(t) \pm \underbrace{\mathbf{q}_b^{\mathrm{T}}\ \mathbf{W}_{m,b}}_{\mathbf{0}} \zeta_b(t) + \underbrace{\mathbf{q}_b^{\mathrm{T}}\ \mathbf{W}_{in,b}}_{\mathbf{0}} \mathbf{u}_{in,b}(t) - \omega_b(t)x_{ic,b}(t), \qquad x_{ic,b}(0) = 1$$

Transformation in variants and invariants

- Condition: rank$([\mathbf{N}_b^{\mathrm{T}}\ \mathbf{W}_{m,b}\ \mathbf{W}_{in,b}\ \mathbf{n}_{0,b}]) = d := R_b + p_m + p_b + 1$

$$\mathbf{x}(t) = \begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_m(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \\ \mathbf{x}_{iv}(t) \end{bmatrix} := \begin{bmatrix} \mathbf{R}_b \\ \mathbf{M}_b \\ \mathbf{F}_b \\ \mathbf{q}_b^{\mathrm{T}} \\ \mathbf{Q}_b \end{bmatrix} \mathbf{n}_b(t) = \mathbf{T}\ \mathbf{n}_b(t) \qquad b \in \{\ell, g\}$$

- Vessel extents (variants) and $q_b = S_b - R_b - p_m - p_b - 1$ invariants

$$\dot{\mathbf{x}}_{r,b}(t) = \mathbf{r}_{v,b}(t) - \omega_b(t)\mathbf{x}_{r,b}(t), \qquad \mathbf{x}_{r,b}(0) = \mathbf{0}_{R_b}$$

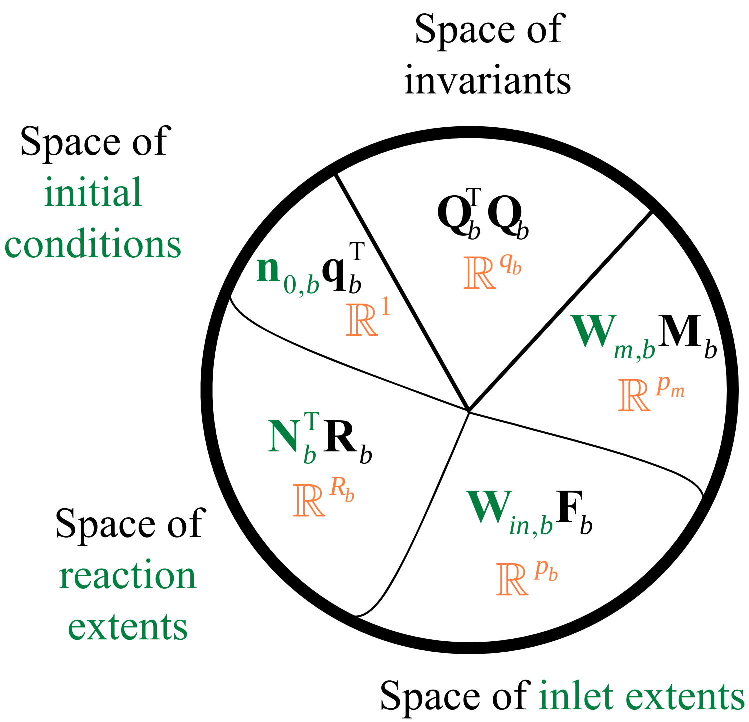
$$\dot{\mathbf{x}}_{m,b}(t) = \zeta_b(t) - \omega_b(t)\mathbf{x}_{m,b}(t), \qquad \mathbf{x}_{m,b}(0) = \mathbf{0}_{p_m}$$

$$\dot{\mathbf{x}}_{in,b}(t) = \mathbf{u}_{in,b}(t) - \omega_b(t)\mathbf{x}_{in,b}(t), \qquad \mathbf{x}_{in,b}(0) = \mathbf{0}_{p_b}$$

$$\dot{x}_{ic,b}(t) = 0 - \omega_b(t)x_{ic,b}(t), \qquad x_{ic,b}(0) = 1, \quad 0 \le x_{ic,b} \le 1 \qquad \mathbf{x}_{iv,b}(t) = \mathbf{Q}_b\mathbf{n}_b(t) = \mathbf{0}_{q_b}$$

$$\mathbf{n}_b(t) = \mathbf{T}^{-1}\mathbf{x}(t) = \mathbf{N}_b^{\mathrm{T}}\mathbf{x}_{r,b}(t) \pm \mathbf{W}_{m,b}\mathbf{x}_{m,b}(t) + \mathbf{W}_{in,b}\mathbf{x}_{in,b}(t) + \mathbf{n}_{0,b}x_{ic,b}(t)$$

Variant and invariant subspaces



S_b dimensional space

$d = R_b + p_m + p_b + 1$ variants

$$\mathbf{T} := \begin{bmatrix} \mathbf{R}_b \\ \mathbf{M}_b \\ \mathbf{F}_b \\ \mathbf{q}_b^{\mathrm{T}} \\ \mathbf{Q}_b \end{bmatrix} = [\mathbf{N}_b^{\mathrm{T}} \;\; \mathbf{W}_{m,b} \;\; \mathbf{W}_{in,b} \;\; \mathbf{n}_{0,b} \;\; \mathbf{P}]^{-1}$$

with $\mathbf{P}^{\mathrm{T}}[\mathbf{N}_b^{\mathrm{T}} \;\; \mathbf{W}_{m,b} \;\; \mathbf{W}_{in,b} \;\; \mathbf{n}_{0,b}] = \mathbf{0}_{q_b \times d}$ (null space)

$$\begin{bmatrix} \mathbf{R}_b \\ \mathbf{M}_b \\ \mathbf{F}_b \\ \mathbf{q}_b^{\mathrm{T}} \\ \mathbf{Q}_b \end{bmatrix} [\mathbf{N}_b^{\mathrm{T}} \;\; \mathbf{W}_{m,b} \;\; \mathbf{W}_{in,b} \;\; \mathbf{n}_{0,b} \;\; \mathbf{P}] = \begin{bmatrix} \mathbf{I}_{R_b} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{I}_{p_m} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{I}_{p_b} & \mathbf{0} & \mathbf{0} \\ 0 & 0 & 0 & 1 & 0 \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{I}_q \end{bmatrix}$$

$$\mathbf{N}_b^{\mathrm{T}}\mathbf{R}_b + \mathbf{W}_{m,b}\mathbf{M}_b + \mathbf{W}_{in,b}\mathbf{F}_b + \mathbf{n}_{0,b}\mathbf{q}_b^{\mathrm{T}} + \mathbf{P}\,\mathbf{Q}_b = \mathbf{I}_{S_b}$$

Transformation to RMV form

- When $\mathrm{rank}([\mathbf{N}_b^{\mathrm{T}}\ \mathbf{W}_{m,b}\ \mathbf{W}_{in,b}\ \mathbf{n}_{0,b}]) < R_b + p_m + p_b + 1$,

  $\mathbf{n}(t)$ can be rearranged in **R**eaction **M**ass-transfer **V**ariant (RMV) form:

$$\mathbf{n}_b^{\mathrm{RMV}}(t) = \mathbf{N}_b^{\mathrm{T}}\mathbf{x}_{r,b}(t) \pm \mathbf{W}_{m,b}\mathbf{x}_{m,b}(t) = \mathbf{n}_b(t) - \mathbf{W}_{in,b}\mathbf{x}_{in,b}(t) - \mathbf{n}_{0,b}x_{ic,b}(t)$$

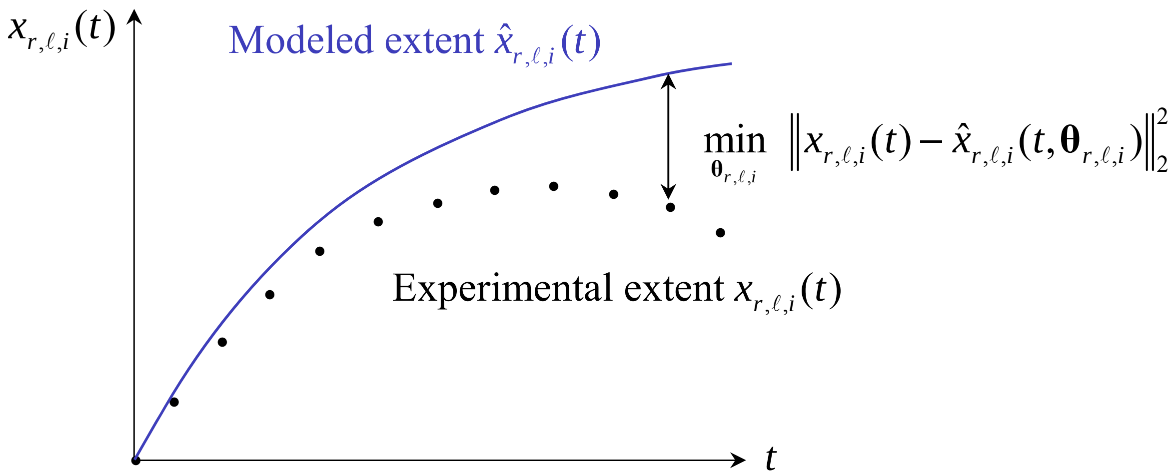
- The **vessel extents** of the R_b reactions and of the p_m mass-transfers are then computed as:

$$\begin{bmatrix} \mathbf{x}_{r,b}(t) \\ \mathbf{x}_{m,b}(t) \end{bmatrix} = [\mathbf{N}_b^{\mathrm{T}}\ \ \pm\mathbf{W}_{m,b}]^{+}\,\mathbf{n}_b^{\mathrm{RMV}}(t)$$

Extent-based model identification

A dynamic model is postulated for each extent of interest and a regression problem is solved individually using the integral method of parameter estimation.

Example: fitting of the i^{th} extent of reaction in phase L



Extent-based model identification

A dynamic model is postulated for each extent of interest and a regression problem is solved individually using the integral method of parameter estimation.

Example: fitting of the i^{th} extent of reaction in phase L

$$\min_{\boldsymbol{\theta}_{r,\ell,i}} \left\| x_{r,\ell,i}(t) - \hat{x}_{r,\ell,i}(t, \boldsymbol{\theta}_{r,\ell,i}) \right\|^2 \qquad i = 1, \ldots, R_\ell$$

$$\text{s.t.} \quad \dot{\hat{x}}_{r,\ell,i}(t, \boldsymbol{\theta}_{r,\ell,i}) = r_{v,\ell,i}(t, \boldsymbol{\theta}_{r,\ell,i}) - \omega_\ell(t)\hat{x}_{r,\ell,i}(t), \qquad \hat{x}_{r,\ell,i}(0) = 0$$

$$\boldsymbol{\theta}^L_{r,\ell,i} \leq \boldsymbol{\theta}_{r,\ell,i} \leq \boldsymbol{\theta}^U_{r,\ell,i}$$

Bhatt et al, Ind. & Eng. Chem. Res. 50 (2011) 12960

Steady-state diffusion
No accumulation in the film

Bulk: $\dot{\mathbf{n}}_g(t) = \mathbf{N}_g^{\mathrm{T}} \dot{\mathbf{x}}_{r,g}(t) - \mathbf{W}_{m,g} \dot{\mathbf{x}}_{m,g}(t) + \mathbf{W}_{in,g} \dot{\mathbf{x}}_{in,g}(t) + \mathbf{n}_{0,g} \dot{x}_{ic,g}(t), \quad \mathbf{n}_g(0) = \mathbf{n}_{0,g}$

Phase G

Phase L

$$\dot{\mathbf{x}}_{m,g}(t) = \zeta(t) - \omega_g(t) \mathbf{x}_{m,g}(t)$$

Film: $\dot{\mathbf{c}}_f(t,z) = \mathbf{D} \frac{\partial}{\partial z^2} \mathbf{c}_f(t,z) + \mathbf{N}_f^{\mathrm{T}} \mathbf{r}_f(t,z) \coloneqq \mathbf{0}_{p_m},$

$$\mathbf{c}_f(t,0) = \mathbf{c}_g^{\star}(t), \quad \mathbf{c}_f(t,\delta) = \mathbf{c}_\ell(t)$$

$$\zeta(t) = \underbrace{\left(\frac{\mathbf{D}}{\delta}\right)}_{\mathbf{k}_m} \left(\mathbf{c}_g^{\star}(t) - \mathbf{c}_\ell(t)\right)$$

$$\dot{\mathbf{x}}_{m,\ell}(t) = \zeta(t) - \omega_\ell(t) \mathbf{x}_{m,\ell}(t)$$

δ

Bulk: $\dot{\mathbf{n}}_\ell(t) = \mathbf{N}_\ell^{\mathrm{T}} \dot{\mathbf{x}}_{r,\ell}(t) + \mathbf{W}_{m,\ell} \dot{\mathbf{x}}_{m,\ell}(t) + \mathbf{W}_{in,\ell} \dot{\mathbf{x}}_{in,\ell}(t) + \mathbf{n}_{0,\ell} \dot{x}_{ic,\ell}(t), \quad \mathbf{n}_\ell(0) = \mathbf{n}_{0,\ell}$

Unsteady-state diffusion
Dynamic accumulation and reaction in the film

Bulk: $$\dot{\mathbf{n}}_g(t) = \mathbf{N}_g^{\mathrm{T}}\dot{\mathbf{x}}_{r,g}(t) - \mathbf{W}_{m,g}\dot{\mathbf{x}}_{m,g}(t) + \mathbf{W}_{in,g}\dot{\mathbf{x}}_{in,g}(t) + \mathbf{n}_{0,g}\dot{x}_{ic,g}(t), \quad \mathbf{n}_g(0) = \mathbf{n}_{0,g}$$

Phase G

Phase L

$$\zeta_g(t) = -\mathbf{D}\tfrac{\partial}{\partial z}\mathbf{c}_f(t)\Big|_{z=0} \qquad \dot{\mathbf{x}}_{m,g}(t) = \zeta_g(t) - \omega_g(t)\mathbf{x}_{m,g}(t)$$

Film: $$\dot{\mathbf{c}}_f(t,z) = \mathbf{D}\tfrac{\partial}{\partial z^2}\mathbf{c}_f(t,z) + \mathbf{N}_f^{\mathrm{T}}\mathbf{r}_f(t,z) \neq \mathbf{0}_{p_m}, \qquad \mathbf{c}_f(t,0) = \mathbf{c}_g^{\star}(t), \quad \mathbf{c}_f(t,\delta) = \mathbf{c}_\ell(t)$$

$$\zeta_\ell(t) = -\mathbf{D}\tfrac{\partial}{\partial z}\mathbf{c}_f(t)\Big|_{z=\delta} \qquad \dot{\mathbf{x}}_{m,\ell}(t) = \zeta_\ell(t) - \omega_\ell(t)\mathbf{x}_{m,\ell}(t)$$

δ

Bulk: $$\dot{\mathbf{n}}_\ell(t) = \mathbf{N}_\ell^{\mathrm{T}}\dot{\mathbf{x}}_{r,\ell}(t) + \mathbf{W}_{m,\ell}\dot{\mathbf{x}}_{m,\ell}(t) + \mathbf{W}_{in,\ell}\dot{\mathbf{x}}_{in,\ell}(t) + \mathbf{n}_{0,\ell}\dot{x}_{ic,\ell}(t), \quad \mathbf{n}_\ell(0) = \mathbf{n}_{0,\ell}$$

Extent-based model identification
Dynamic accumulation w/o reaction in the film

The diffusion equation (PDE) and the fluxes (ODEs) at the boundaries are integrated to obtain the extents of mass transfer in the bulks of each phase, and a regression problem is solved individually for each extent.

Example: fitting of the j^{th} pair of extents of mass transfer (in G and L)

$$\min_{D_j,\delta} \; w\left\|x_{m,\ell,j}(t)-\hat{x}_{m,\ell,j}(t,D_j,\delta)\right\|^2+(1-w)\left\|x_{m,g,j}(t)-\hat{x}_{m,g,j}(t,D_j,\delta)\right\|^2$$

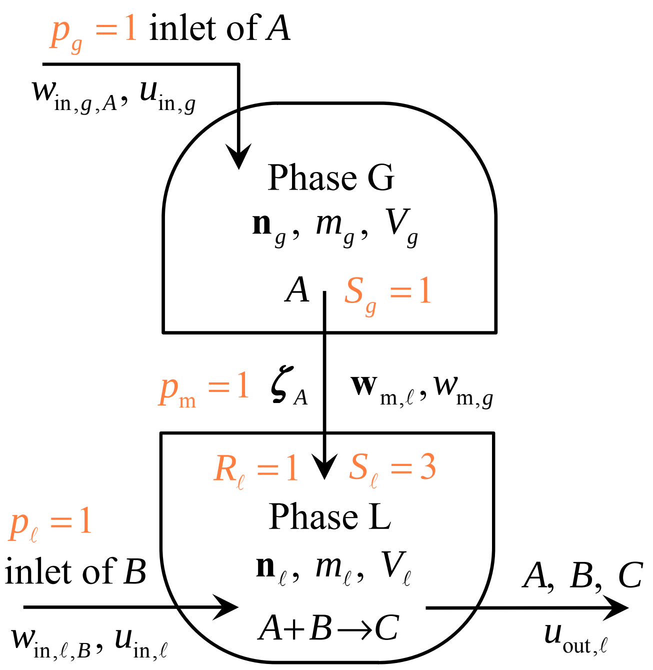
$$\text{s.t.} \quad \dot{\hat{c}}_{f,j}(t,z)=D_j \tfrac{\partial}{\partial z^2} c_{f,j}(t,z), \qquad c_{f,j}(t,0)=c^{\star}_{g,j}(t), \quad c_{f,j}(t,\delta)=c_{\ell,j}(t)$$

$$\dot{\hat{x}}_{m,g,j}(t)=-D_j \tfrac{\partial}{\partial z} c_{f,j}(t)\Big|_{z=0}-\omega_g(t)x_{m,g,j}(t), \qquad \hat{x}_{m,g,j}(0)=0$$

$$\dot{\hat{x}}_{m,\ell,j}(t)=-D_j \tfrac{\partial}{\partial z} c_{f,j}(t)\Big|_{z=\delta}-\omega_\ell(t)x_{m,\ell,j}(t), \qquad \hat{x}_{m,\ell,j}(0)=0 \qquad j=1,\ \ldots,\ p_m$$

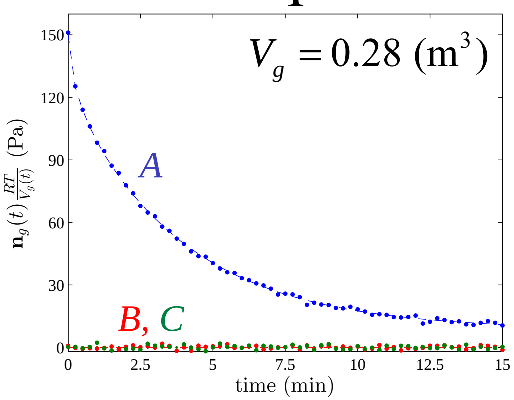
Case study 1
Unsteady state diffusion (1 diffusing species)

- Species A enters phase G and transfers to phase L to react in the bulk with dosed species B and form species C
- The film is initially at steady state
- In phase G, $p_m + p_g > S_g$ (no reaction), data are to be treated in **M**ass-transfer **V**ariant (MV) form
- In phase L, $R_\ell + p_m + p_\ell + 1 > S_\ell$ and data are to be treated in **R**eaction **M**ass-transfer **V**ariant (RMV) form



Case study 1
Unsteady state diffusion (1 diffusing species)

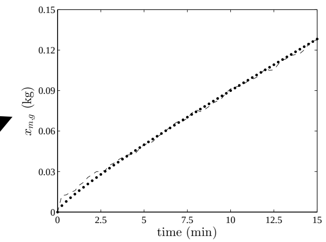
Bulk of phase G



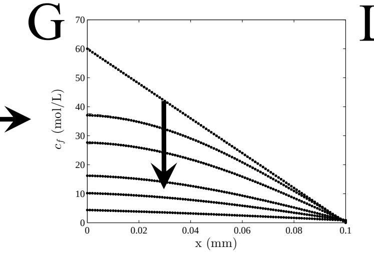
$w_{\text{in},g,A}$, $u_{\text{in},g}$

$$x_{m,g} = -\mathbf{w}_{m,g}^{+}\mathbf{n}_g^{\text{MV}}$$

Extent of m.t. (in G)

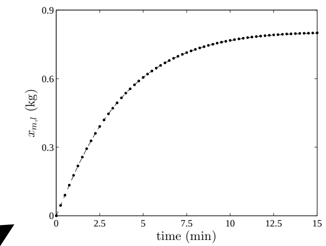


Concentration in the film



Solution of Fick's law

Extent of m.t. (in L)



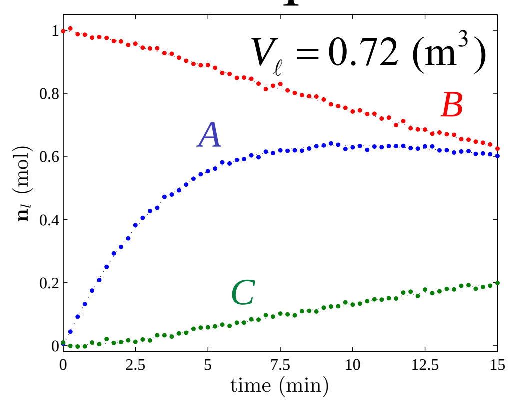
δ = 0.1 (mm), True value: 0.1

D_A = 9.95 (±10)·10^{-10} (m^2/s)

True value: 10^{-9}

$\rho(\delta, D_A)$ = -0.65

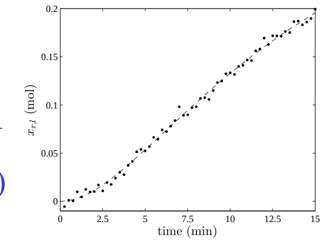
Bulk of phase L



$w_{\text{in},\ell,B}$, $u_{\text{in},\ell}$, $u_{out,\ell}$

$$\begin{bmatrix} x_{r,\ell} \\ x_{m,\ell} \end{bmatrix} = [\mathbf{N}_\ell^{\text{T}} \ \mathbf{w}_{m,\ell}]^{+}\mathbf{n}_\ell^{\text{RMV}}$$

Extent of reaction

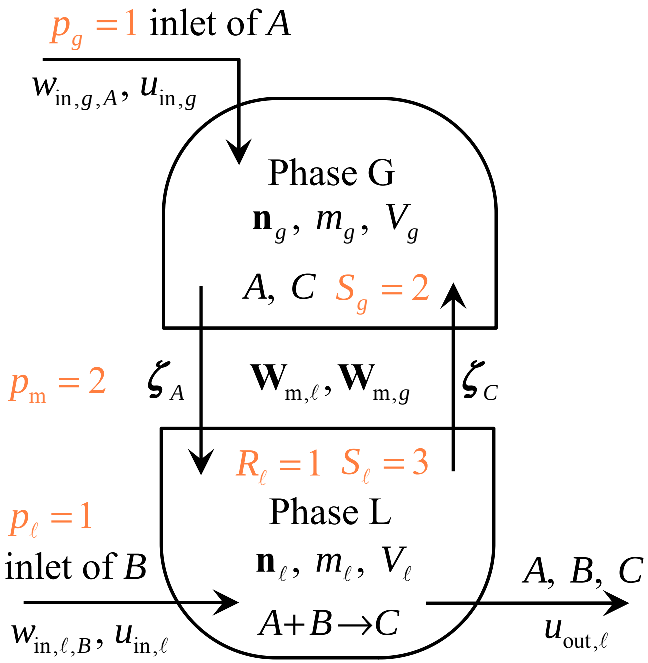


k = 0.0249 ± 0.0003 (L/mol·min)

True value: 0.0250

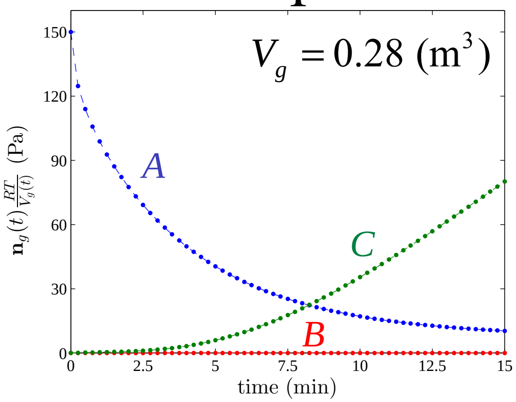
Case study 2
Unsteady state diffusion (2 diffusing species)

- Same diffusion-reaction system as in Case study 1, with species *C* transferring to phase G
- The film is initially at steady state
- In phase G, $p_m + p_g > S_g$ (no reaction), data are to be treated in **M**ass-transfer **V**ariant (MV) form
- In phase L, $R_\ell + p_m + p_\ell + 1 > S_\ell$ and data are to be treated in **R**eaction **M**ass-transfer **V**ariant (RMV) form



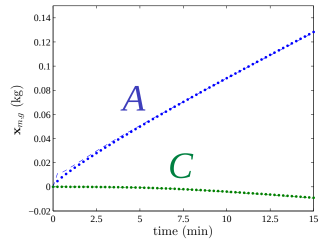
Case study 2
Unsteady state diffusion (2 diffusing species)

Bulk of phase G

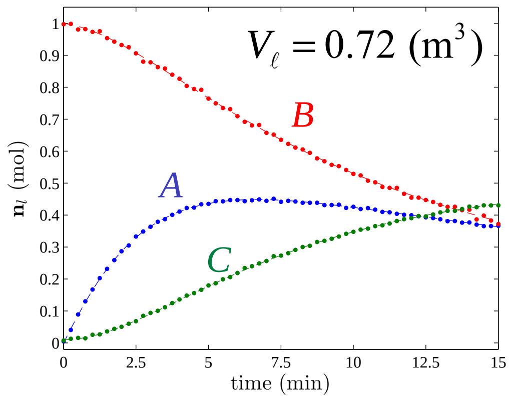


$$\mathbf{x}_{m,g} = -\mathbf{W}_{m,g}^{+}\mathbf{n}_g^{\mathrm{MV}}$$

Extent of m.t. (in G)

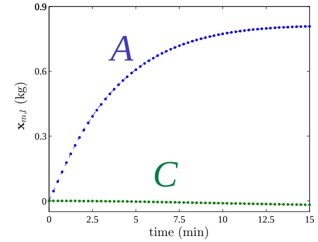


Bulk of phase L



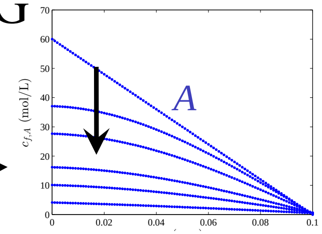
$$\begin{bmatrix} x_{r,\ell} \\ \mathbf{x}_{m,\ell} \end{bmatrix} = [\mathbf{N}_\ell^{\mathrm{T}} \ \ \mathbf{W}_{m,\ell}]^{+}\mathbf{n}_\ell^{\mathrm{RMV}}$$

Extent of m.t. (in L)

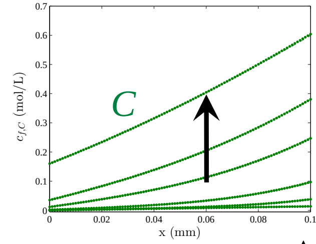


Concentration in the film

G L



$\delta = 0.100$ (mm),
$D_A = 1.00\ (\pm 100)\cdot 10^{-9}$ (m^2/s)
$\rho(\delta, D_A) = +0.88$



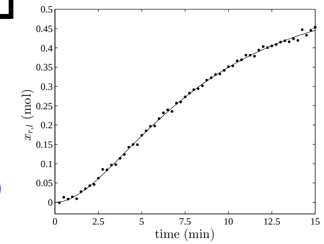
$\delta = 0.105$ (mm),
$D_A = 1.10\ (\pm 40)\cdot 10^{-9}$ (m^2/s)
$\rho(\delta, D_A) = -0.98$

Solution of Fick's law

Extent of reaction

$k = 0.1002 \pm 0.0002$ (L/mol·min)

True value: 0.1000



Conclusion

- This work represents a first attempt describing the incremental identification of reaction systems with dynamic accumulation (and reactions) in a diffusion layer.
- Using a transformation to extents, reaction parameters estimated incrementally in bulk phases are not affected by a poor modeling of the diffusion layer.
- An accurate estimation of reaction and diffusion parameters within the film remains a challenge.
- Future work will focus on the development of a transformation to separate mathematically the diffusion, convection and reaction phenomena in distributed systems (e.g. tubular reactors, PFR).

Thank you for your attention

Model reduction

- M. Amrhein, PhD dissertation n°1861 (1998), EPFL, Switzerland
- Bhatt et al., Comp. & Chem. Eng. (2011), submitted

Transformation to variants/invariants (extents)

- Amrhein et al., AIChE J. 56 (2010) 2873
- N. Bhatt, PhD dissertation n°5028 (2011), EPFL, Switzerland
- Srinivasan et al., IFAC Workshop (TFMST), Lyon, July 13–16, 2013

Incremental model identification

- Bhatt et al., Ind. & Eng. Chem. Res. 49 (2010) 7704
- Bhatt et al., Ind. & Eng. Chem. Res. 50 (2011) 12960
- Bhatt et al., Chem. Eng. Sci. 8 (2012) 24

Rank augmentation by calorimetric data

- Srinivasan et al., Chem. Eng. J. 207-208 (2012) 785

Incremental kinetic modeling of spectroscopic data

- Billeter et al., Anal. Chim. Acta 767 (2013) 21