Incremental Identification of Reaction Systems

Minimal Number of Measurements

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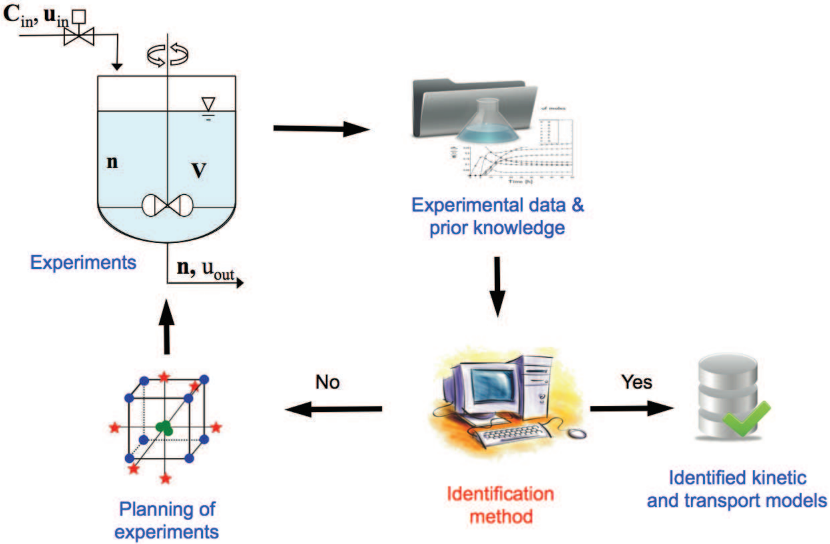
Outline

- Identification of reaction systems from measured data
  - Simultaneous or incremental approach?
  - Number of measurements for incremental identification?
- Minimal state representation
  - Homogeneous w/o outlet (batch, semi-batch) $\longrightarrow$ extents of reaction
  - Homogeneous with outlet $\longrightarrow$ vessel extents of reaction
  - Gas-liquid with outlet $\longrightarrow$ vessel extents of reaction and mass transfer
- Number of measurements for full state reconstruction
  - Gas-liquid reaction system with outlet
- Conclusions



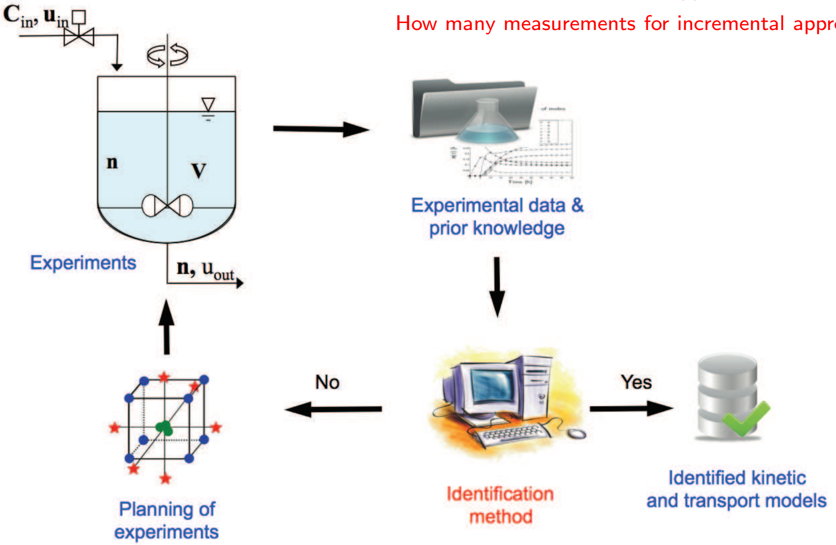
C_{in}, u_{in}
n
V
Experiments
n, u_{out}
Experimental data &
prior knowledge
No
Yes
Planning of
experiments
Identification
method
Identified kinetic
and transport models

Context – Kinetic investigation

Iterative procedure

Issues: Simultaneous or incremental approach?

How many measurements for incremental approach?



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

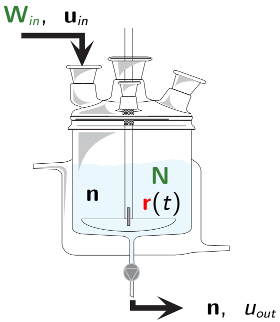
Mole balances for S species

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

(S) $(S \times R)$ (R) $(S \times p)$ (p)

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

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



Global macroscopic view

Generally valid regardless of temperature, catalyst, solvent, etc.

Gas-liquid reaction systems

Balance equations

- Assumptions
  - the gas and liquid phases are homogeneous
  - the reactions take place in the liquid bulk only
  - no accumulation in the boundary layer

Liquid phase

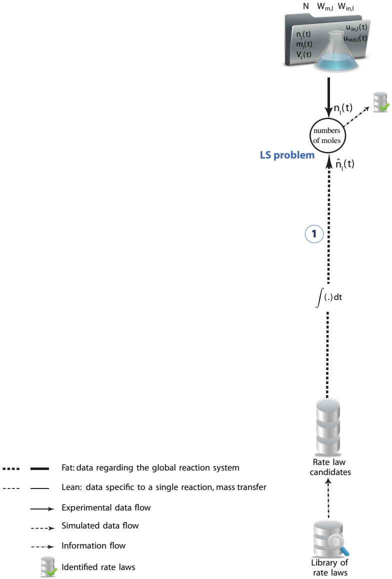
$$\underset{(S_l)}{\dot{\mathbf{n}}_l(t)} = \underset{(S_l \times R_l)}{\mathbf{N}^{\mathrm{T}}} V_l(t) \underset{(R_l)}{\mathbf{r}(t)} + \underset{(S_l \times p_l)}{\mathbf{W}_{m,l}} \underset{(p_l)}{\zeta(t)} + \underset{(S_l \times p_m)}{\mathbf{W}_{in,l}} \underset{(p_m)}{\mathbf{u}_{in,l}(t)} - \frac{u_{out,l}(t)}{m_l(t)} \mathbf{n}_l(t), \quad \mathbf{n}_l(0) = \mathbf{n}_{l0}$$

Gas phase

$$\underset{(S_g)}{\dot{\mathbf{n}}_g(t)} = -\underset{(S_g \times p_g)}{\mathbf{W}_{m,g}} \underset{(p_g)}{\zeta(t)} + \underset{(S_g \times p_m)}{\mathbf{W}_{in,g}} \underset{(p_m)}{\mathbf{u}_{in,g}(t)} - \frac{u_{out,g}(t)}{m_g(t)} \mathbf{n}_g(t), \quad \mathbf{n}_g(0) = \mathbf{n}_{g0}$$

From measured data to rate expressions

Simultaneous approach



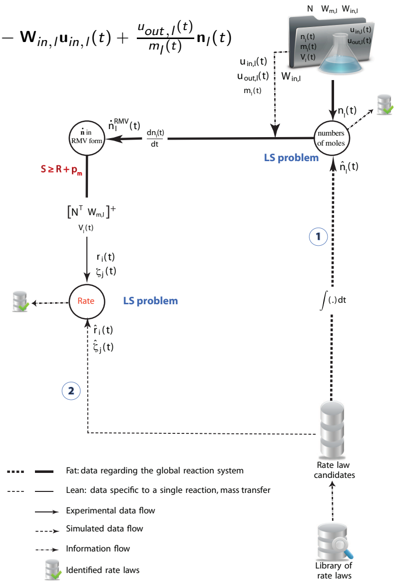
Number of measurements
as required for identifiability

1 **Simultaneous approach**

From measured data to rate expressions

Incremental rate-based approach

$$\dot{\mathbf{n}}_l^{RMV}(t) = \dot{\mathbf{n}}_l(t) - \mathbf{W}_{in,l}\mathbf{u}_{in,l}(t) + \frac{u_{out,l}(t)}{m_l(t)}\mathbf{n}_l(t)$$



at least $R + p_m$ measurements

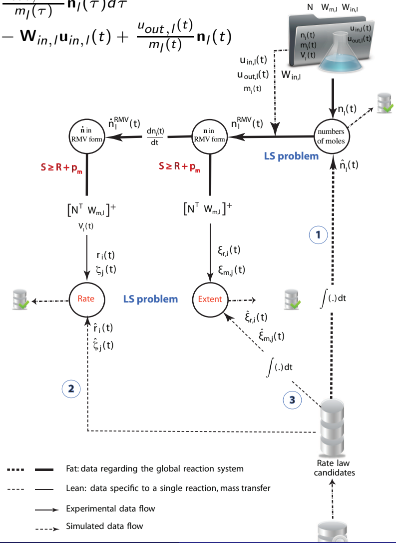
1. **Simultaneous approach**
2. **Incremental rate-based approach**

From measured data to rate expressions

Incremental extent-based approach

$$\mathbf{n}_l^{RMV}(t) = \mathbf{n}_l(t) - \mathbf{n}_{l0} - \mathbf{W}_{in,l}\int_0^t \mathbf{u}_{in,l}(\tau)d\tau + \int_0^t \frac{u_{out,l}(\tau)}{m_l(\tau)}\mathbf{n}_l(\tau)d\tau$$

$$\dot{\mathbf{n}}_l^{RMV}(t) = \dot{\mathbf{n}}_l(t) - \mathbf{W}_{in,l}\mathbf{u}_{in,l}(t) + \frac{u_{out,l}(t)}{m_l(t)}\mathbf{n}_l(t)$$



at least R + p_m measurements

1. **Simultaneous approach**
2. **Incremental rate-based approach**

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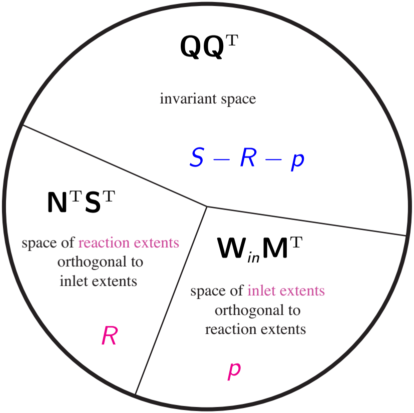
- Application – Kinetic Identification
  - Simultaneous approach
  - Incremental approaches
- Conclusions



S-dimensional space, $R + p$ variants

$$\begin{bmatrix} \mathbf{S}^{\mathrm{T}} \\ \mathbf{M}^{\mathrm{T}} \end{bmatrix} = \begin{bmatrix} \mathbf{N}^{\mathrm{T}} & \mathbf{W}_{in} \end{bmatrix}^{+}$$

$\mathbf{Q}$ orthogonal to $\mathbf{N}^{\mathrm{T}}$ and $\mathbf{W}_{in}$

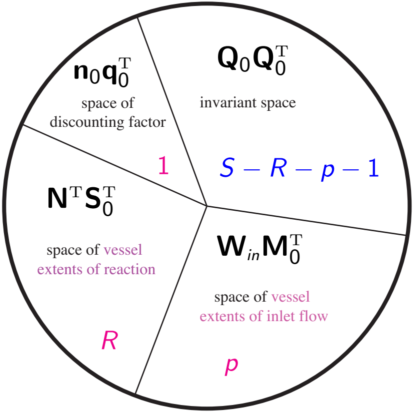
$$\dot{\xi}_{r,i}(t) = V(t)\, r_i(t) \qquad \xi_{r,i}(0) = 0$$

$$\dot{\xi}_{in,j}(t) = u_{in,j}(t) \qquad \xi_{in,j}(0) = 0$$

$$\boldsymbol{\xi}_{iv} = \mathbf{Q}^{\mathrm{T}}(\mathbf{n} - \mathbf{n}_0) = \mathbf{0}_{S-R-p}$$

$$\mathbf{n}(t) = \mathbf{N}^{\mathrm{T}}\boldsymbol{\xi}_r(t) + \mathbf{W}_{in}\boldsymbol{\xi}_{in}(t)$$

Amrhein et al. (2010), AIChE Journal, 56(11), 2873-2886.



S-dimensional space, $R+p+1$ variants

$$\begin{bmatrix} \mathbf{S}_0^{\mathrm{T}} \\ \mathbf{M}_0^{\mathrm{T}} \\ \mathbf{q}_0^{\mathrm{T}} \end{bmatrix} = \begin{bmatrix} \mathbf{N}^{\mathrm{T}} & \mathbf{W}_{in} & \mathbf{n}_0 \end{bmatrix}^{+}$$

$\mathbf{Q}_0$ orthogonal to $\mathbf{N}^{\mathrm{T}}$, $\mathbf{W}_{in}$ and $\mathbf{n}_0$

$$\dot{x}_{r,i} = V\, r_i - \frac{u_{out}}{m}\, x_{r,i} \qquad x_{r,i}(0) = 0$$

$$\dot{x}_{in,j} = u_{in,j} - \frac{u_{out}}{m}\, x_{in,j} \qquad x_{in,j}(0) = 0$$

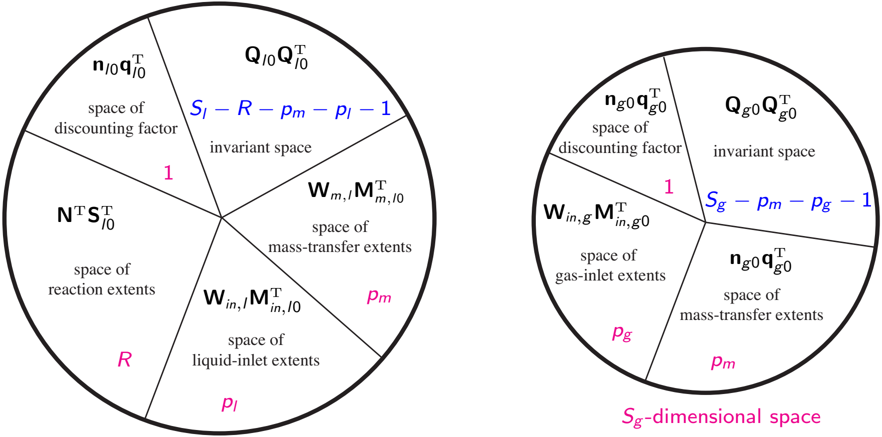
$$\dot{\lambda} = -\frac{u_{out}}{m}\, \lambda \qquad \lambda(0) = 1$$

$$\mathbf{x}_{iv} = \mathbf{Q}_0^{\mathrm{T}}\,\mathbf{n} = \mathbf{0}_{S-R-p-1}$$

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

[1] Bhatt et al. (2010), *I&EC Research*, 49:7704-7717

Orthogonal spaces in five-way and four-way decomposition



S_l-dimensional space
$R + p_m + p_l + 1$ variants

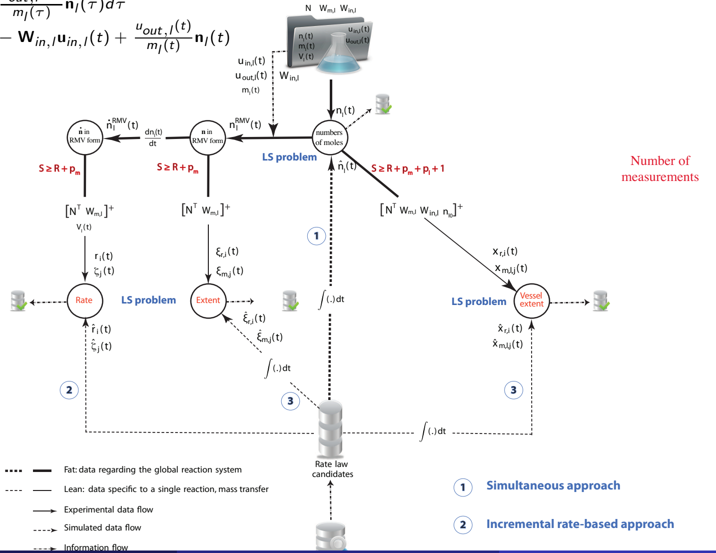
S_g-dimensional space
$p_m + p_g + 1$ variants

Dimensionality of the dynamic model: $(R + 2p_m + p_l + p_g + 2)$ and not $(S_l + S_g)$

Bhatt et al. (2010), I&EC Research, 49(17), 7704-7717.

$$\mathbf{n}_l^{RMV}(t) = \mathbf{n}_l(t) - \mathbf{n}_{l0} - \mathbf{W}_{in,l}\int_0^t \mathbf{u}_{in,l}(\tau)d\tau + \int_0^t \frac{u_{out,l}(\tau)}{m_l(\tau)}\mathbf{n}_l(\tau)d\tau$$

$$\dot{\mathbf{n}}_l^{RMV}(t) = \dot{\mathbf{n}}_l(t) - \mathbf{W}_{in,l}\mathbf{u}_{in,l}(t) + \frac{u_{out,l}(t)}{m_l(t)}\mathbf{n}_l(t)$$



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The idea is to estimate p_{m_g} mass-transfer rates from gas-phase measurements and p_{m_l} from liquid-phase measurements, with $p_{m_g} + p_{m_l} = p_m$

- Gas phase

$$\tilde{\mathbf{n}}_g^{MV}(t) = \mathbf{n}_g(t) - \mathbf{W}_{in,g}\,\mathbf{x}_{in,g}(t) - \mathbf{n}_{g0}\,\lambda_g(t)$$

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

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

$$\mathbf{x}_{m_g,g}(t) = -(\mathbf{W}_{m_g,g})^{+}\,\tilde{\mathbf{n}}_g^{MV}(t)$$

which requires measurements of p_{m_g} numbers of moles, $\mathbf{u}_{in,g}(t)$ and $u_{out,g}(t)$

Number of measurements for full state reconstruction

Gas-liquid reaction systems, unknown rate expressions $\mathbf{r}(t)$ and $\zeta(t)$

- Liquid phase

$$\mathbf{x}_{m_g,l}(t) = \mathbf{x}_{m_g,g}(t) - \boldsymbol{\delta}_{m_g}(t)$$

$$\dot{\boldsymbol{\delta}}_{m_g} = -\frac{u_{out,l}}{m_l}\boldsymbol{\delta}_{m_g} + \left(\frac{u_{out,l}}{m_l} - \frac{u_{out,g}}{m_g}\right)\mathbf{x}_{m_g} \qquad \boldsymbol{\delta}_{m_g}(0) = \mathbf{0}_{p_{m_g}}$$

$$\tilde{\mathbf{n}}_l^{RMV}(t) = \mathbf{n}_l(t) - \mathbf{W}_{in,l}\,\mathbf{x}_{in,l}(t) - \mathbf{n}_{l0}\,\lambda_l(t) - \mathbf{W}_{m_g,l}\,\mathbf{x}_{m_g,l}(t)$$

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

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

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{m_l,l}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{N}^{\mathrm{T}} & \mathbf{W}_{m_l,l} \end{bmatrix}^{+} \tilde{\mathbf{n}}_l^{RMV}(t)$$

which requires measurements of $R + p_{m_l}$ numbers of moles, $\mathbf{u}_{in,g}(t)$ and $u_{out,g}(t)$

- Total number of measurements

$R + p_{m_l} + p_{m_g} = R + p_m$ numbers of moles plus the inlet and outlet flows

From measured data to rate expressions

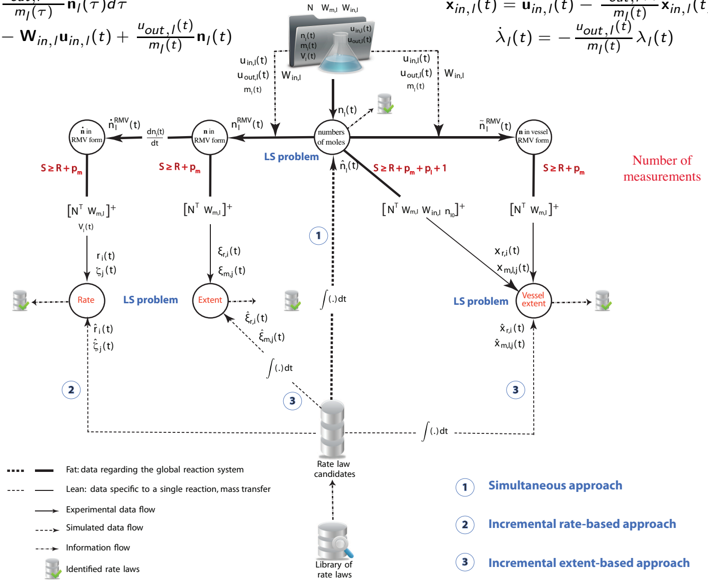
$$\mathbf{n}_l^{RMV}(t) = \mathbf{n}_l(t) - \mathbf{n}_{l0} - \mathbf{W}_{in,l}\int_0^t \mathbf{u}_{in,l}(\tau)d\tau + \int_0^t \frac{u_{out,l}(\tau)}{m_l(\tau)}\mathbf{n}_l(\tau)d\tau$$

$$\dot{\mathbf{n}}_l^{RMV}(t) = \dot{\mathbf{n}}_l(t) - \mathbf{W}_{in,l}\mathbf{u}_{in,l}(t) + \frac{u_{out,l}(t)}{m_l(t)}\mathbf{n}_l(t)$$

$$\tilde{\mathbf{n}}_l^{RMV}(t) = \mathbf{n}_l(t) - \mathbf{W}_{in,l}\mathbf{x}_{in,l}(t) - \mathbf{n}_{l0}\lambda_l(t)$$

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

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



1 **Simultaneous approach**

2 **Incremental rate-based approach**

3 **Incremental extent-based approach**

From measured data to rate expressions

$$\mathbf{n}_l^{RMV}(t) = \mathbf{n}_l(t) - \mathbf{n}_{l0} - \mathbf{W}_{in,l}\int_0^t \mathbf{u}_{in,l}(\tau)d\tau + \int_0^t \frac{u_{out,l}(\tau)}{m_l(\tau)}\mathbf{n}_l(\tau)d\tau$$

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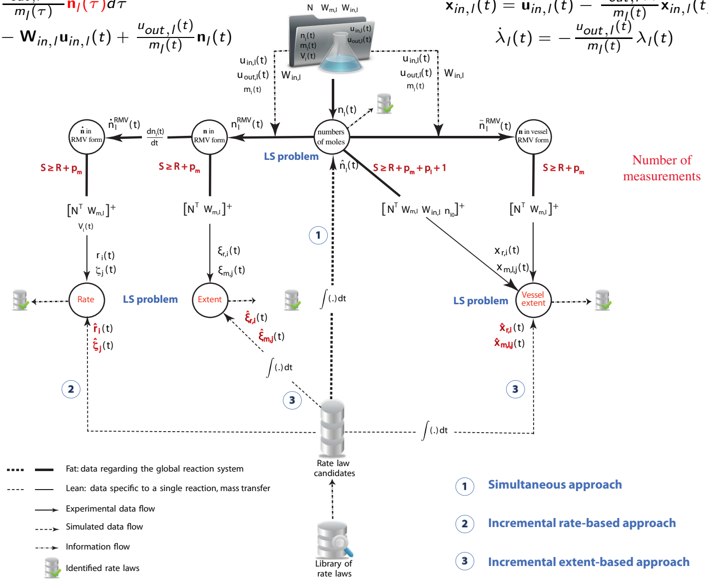
$$\dot{\mathbf{x}}_{in,l}(t) = \mathbf{u}_{in,l}(t) - \frac{u_{out,l}(t)}{m_l(t)}\mathbf{x}_{in,l}(t) \qquad \mathbf{x}_{in,l}(0) = \mathbf{0}$$

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

Difficulty

Differentiation or integration of noisy and scarce data



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Conclusions

- Incremental approaches allow dealing with each rate individually
  - Rate-based approach
    - computation of $\mathbf{n}_l^{RMV}$ using flow measurements
    - *differentiation of sparse and noisy data*
    - requires measurement of $R + p_m$ quantities
  - Extent-based approach
    - computation of $\mathbf{n}_l^{RMV}$ using flow measurements
    - requires measurement of $R + p_m$ quantities
  - Vessel-extent-based approach
    - transformation of $\mathbf{n}_l$ requires measurement of $R + p_m + p_l + 1$ quantities
    - computation of $\mathbf{n}_l^{RMV}$ requires measurement of $R + p_m$ quantities
- Need for additional measurements
  - Calorimetry, gas consumption
  - Spectroscopic measurements
    - via calibration, calibration-free?