Variant and Invariant States for Reaction Systems

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Outline

- Concept of Variants and Invariants

- Concept of Vessel Extents
  - Each extent linked to the corresponding rate process
  - Presence of outlet(s) $\rightarrow$ vessel extents
  - Vessel extents of reaction, mass transfer, heat transfer

- Applications
  - Model reduction
  - Static state reconstruction
  - Incremental kinetic identification

- Conclusions

Homogeneous reaction systems
Balance equations

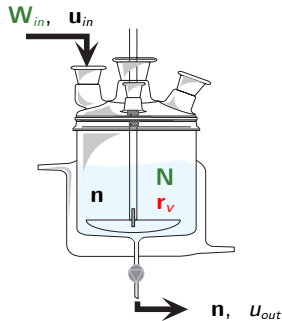Homogeneous reaction system consisting of S species, R independent reactions, p inlet streams, and 1 outlet stream

Mole balances for S species

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

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

$\mathbf{r}_v(t) = V(t)\, \mathbf{r}(t)$ considered as endogenous signal

$\omega(t) = \frac{u_{out}(t)}{m(t)}$

Global macroscopic view

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

$\mathbf{W}_{in}$, $\mathbf{u}_{in}$

$\mathbf{N}$
$\mathbf{n}$
$\mathbf{r}_v$

$\mathbf{n}$, u_{out}

- Linear transformation using $\mathbf{N}$:

$$\begin{bmatrix} \mathbf{y}_r(t) \\ \mathbf{y}_{iv}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{N}^{\mathrm{T}+} \\ \mathbf{P}^{\mathrm{T}} \end{bmatrix} \mathbf{n}(t) \qquad \text{with} \qquad \mathbf{N}\,\mathbf{P} = \mathbf{0}_{\mathrm{R}\times(\mathrm{S}-\mathrm{R})}$$

- Reaction variants $\mathbf{y}_r$ and reaction invariants $\mathbf{y}_{iv}$ describe the reactor state:

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

  - $\mathbf{y}_r$ are reaction and flow variants
  - $\mathbf{y}_{iv}$ are reaction invariants but flow variants
  - $\mathbf{y}_r$ are pure reaction variants and $\mathbf{y}_{iv}$ are true invariants only for batch reactors (with $\mathbf{u}_{in} = \mathbf{0}$, $\omega = 0$)

- Can we compute pure reaction variants and true invariants for open reactors?

[1] Asbjornsen et al. (1970), *Chem. Eng. Sci.*, 25:1627-1639.

Vessel extents and true invariants

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

$$\mathbf{x}(t) := \begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \\ \mathbf{x}_{iv}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{R} \\ \mathbf{F} \\ \mathbf{c}^{\mathrm{T}} \\ \mathbf{Q} \end{bmatrix} \mathbf{n}(t) = \mathcal{T}\, \mathbf{n}(t)$$

- Vessel extents of reaction $\mathbf{x}_r$ and flow $\mathbf{x}_{in}$, discounting factor x_{ic}, and invariants $\mathbf{x}_{iv}$:

$$\dot{\mathbf{x}}_r(t) = \underbrace{\mathbf{R}\mathbf{N}^{\mathrm{T}}}_{\mathbf{I}_R} \mathbf{r}_v(t) + \underbrace{\mathbf{R}\mathbf{W}_{in}}_{\mathbf{0}} \mathbf{u}_{in}(t) - \omega(t)\,\mathbf{x}_r(t) \qquad \mathbf{x}_r(0) = \mathbf{0}_R$$
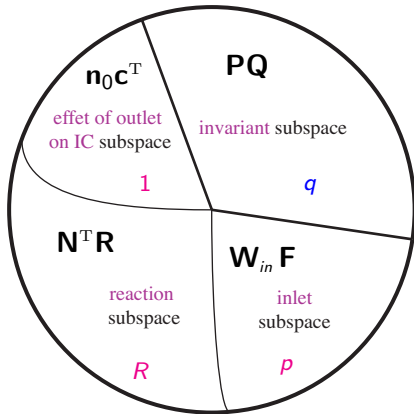
$$\dot{\mathbf{x}}_{in}(t) = \underbrace{\mathbf{F}\mathbf{N}^{\mathrm{T}}}_{\mathbf{0}} \mathbf{r}_v(t) + \underbrace{\mathbf{F}\mathbf{W}_{in}}_{\mathbf{I}_p} \mathbf{u}_{in}(t) - \omega(t)\,\mathbf{x}_{in}(t) \qquad \mathbf{x}_{in}(0) = \mathbf{0}_p$$

$$\dot{x}_{ic}(t) = \underbrace{\mathbf{c}^{\mathrm{T}}\mathbf{N}^{\mathrm{T}}}_{\mathbf{0}} \mathbf{r}_v(t) + \underbrace{\mathbf{c}^{\mathrm{T}}\mathbf{W}_{in}}_{\mathbf{0}} \mathbf{u}_{in}(t) - \omega(t)\,x_{ic}(t) \qquad x_{ic}(0) = 1$$

$$\dot{\mathbf{x}}_{iv}(t) = \underbrace{\mathbf{Q}\mathbf{N}^{\mathrm{T}}}_{\mathbf{0}} \mathbf{r}_v(t) + \underbrace{\mathbf{Q}\mathbf{W}_{in}}_{\mathbf{0}} \mathbf{u}_{in}(t) - \omega(t)\,\mathbf{x}_{iv}(t) \qquad \mathbf{x}_{iv}(0) = \mathbf{0}_q$$

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

Four subspaces

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

$$\mathbf{x}(t) = \mathcal{T}\,\mathbf{n}(t) \qquad \mathcal{T} = \left[\mathbf{N}^{\mathrm{T}}\ \mathbf{W}_{in}\ \mathbf{n}_0\ \mathbf{P}\right]^{-1}$$

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

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

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

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

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

amount that is still in the reactor

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

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

# Homogeneous CSTR – Experimental data

- Ethanolysis reaction with seven species ($S = 7$), three reactions ($R = 3$), two inlets ($p = 2$) and one outlet

- Stoichiometric matrix ($\mathbf{N}$) and inlet-composition matrix ($\mathbf{W}_{in}$):

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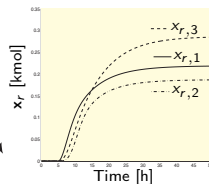

Measured numbers of moles
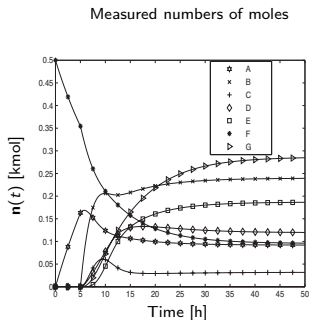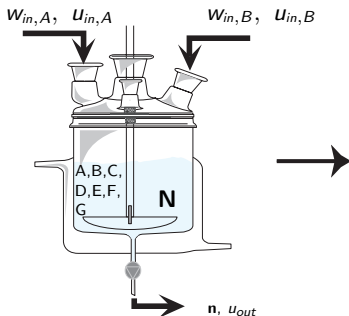
Reaction extents ?

Homogeneous CSTR – Computation of extents

Numbers of moles
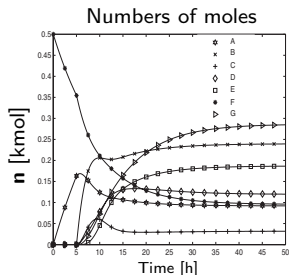
Extents of reaction

Extents of inlet

Effect of outlet on IC

$$\mathcal{T} = \begin{bmatrix} \mathbf{R} \\ \mathbf{F} \\ \mathbf{c}^{\mathrm{T}} \\ \mathbf{Q} \end{bmatrix}$$

$\mathbf{N}$ $\mathbf{W}_{in}$ $\mathbf{n}_0$

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

For one of the phases

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

$$\dot{\mathbf{x}}_m(t) = \boldsymbol{\zeta}(t) - \omega(t)\,\mathbf{x}_m(t) \quad \mathbf{x}_m(0) = \mathbf{0}_{p_m}$$

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

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

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

$$\mathbf{n}(t) = \mathbf{N}^{\mathrm{T}}\,\mathbf{x}_r(t) + \mathbf{W}_m\,\mathbf{x}_m(t) + \mathbf{W}_{in}\,\mathbf{x}_{in}(t) + \mathbf{n}_0\,x_{ic}(t)$$
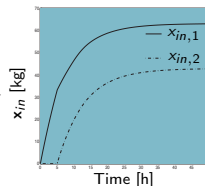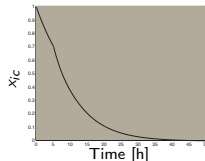
[1] Bhatt et al. (2010), *I&EC Research*, 49:7704-7717

Extension to reaction systems with heat balance equation

$$\mathbf{x}(t) := \mathcal{T} \begin{bmatrix} \mathbf{n}(t) \\ m(t)\, c_p\, T(t) \end{bmatrix} \qquad \text{dimension } S+1$$

- "Decoupled" system

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \omega(t)\, \mathbf{x}_r(t) \qquad\qquad \mathbf{x}_r(0) = \mathbf{0}_R$$
$$\dot{x}_{ex}(t) = q_{ex}(t) - \omega(t)\, x_{ex}(t) \qquad\qquad x_{ex}(0) = 0$$
$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) - \omega(t)\, \mathbf{x}_{in}(t) \qquad\qquad \mathbf{x}_{in}(0) = \mathbf{0}_p$$
$$\dot{x}_{ic}(t) = -\omega(t)\, x_{ic}(t) \qquad\qquad x_{ic}(0) = 1$$
$$\mathbf{x}_{iv} = \mathbf{0}_q$$

- Application: estimation of $q_{ex}(t)$ or identification of heat-transfer coefficients independently of any kinetic information

Model reduction

- Dimensionality

  - $d := R + p + 1, \quad \min(S, d)$ differential equations

  - However, transformation assumes knowledge of $\mathbf{n}_0$, i.e., S initial conditions

- Elimination of fast modes via singular perturbation

  The reactions (and not the associated numbers of moles) exhibit fast or slow dynamic behavior

  $\rightarrow$ transformed decoupled model is well suited for input estimation:

  $$\dot{x}_{r,i}(t) = r_{v,i}(t) - \omega(t)\, x_{r,i}(t) \qquad x_{r,i}(0) = 0$$
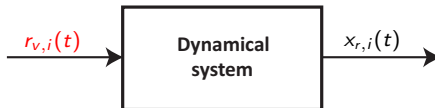
Incremental kinetic identification via rates or extents
Computation of rates and extents

- Rates

$$r_{v,i}(t) = \left(\mathbf{N}^{\mathrm{T}^\dagger}\right)_i \dot{\mathbf{n}}_a^{RV}(t) \qquad \text{(at least } R \text{ measured species)}$$

  with $\dot{\mathbf{n}}_a^{RV}(t) = \dot{\mathbf{n}}_a(t) - \mathbf{W}_{in,a}\,\mathbf{u}_{in}(t) + \omega(t)\,\mathbf{n}_a(t)$

  $\rightarrow$ differentiation of sparse and noisy signal $\mathbf{n}_a(t)$

- Vessel extents

$$x_{r,i}(t) = \left(\mathbf{N}^{\mathrm{T}^\dagger}\right)_i \mathbf{n}_a^{vRV}(t) \qquad \text{(at least } R \text{ measured species)}$$

  with $\mathbf{n}_a^{vRV}(t) := \mathbf{n}_a(t) - \mathbf{W}_{in,a}\,\mathbf{x}_{in}(t) - \mathbf{n}_{0,a}\,x_{ic}(t)$

$$x_{r,i}(t) = \mathbf{R}_i\,\mathbf{n}_a(t) \qquad \text{(at least } R+p+1 \text{ measured species)}$$

  $\rightarrow$ neither integration nor differentiation of the sparse and noisy signal $\mathbf{n}_a(t)$

Conclusions

- Transformation of numbers of moles to "decoupled" vessel extents
  - Transformation uses structural information $\mathbf{N}, \mathbf{W}_{in}, \mathbf{W}_m$ and knowledge of $\mathbf{n}_0$
  - Effect of outlets is accounted for $\rightarrow$ concept of vessel extent
  - Rates considered as time signals, e.g. $\mathbf{r}_v(t)$ and not $\mathbf{r}_v(\mathbf{c}, T)$

- Possible applications
  - Homogeneous and fluid-fluid reaction systems
    - Model reduction
    - Static state reconstruction
    - Incremental kinetic identification
  - Heterogeneous catalytic reaction systems?
  - Distributed reaction systems?