Extent-based Incremental Identification of Reaction Kinetics from Spectroscopic Data

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Kinetic investigation
From data to rate expressions

Experiments, measurements and required information

1. Computation of extents
2. Individual identification of rate expressions
3. Estimation of rate parameters

- Simultaneous approach
- Incremental approach rate-based
- Incremental approach extent-based

1. Computation of extents
2. Individual identification of rate expressions
3. Estimation of rate parameters

(number of measured species) = (number of computed extents)

(number of measured species) = (number of computed rates)
Homogeneous reaction systems
Balance equations

Homogeneous reaction system containing $S$ species, $R$ independent reactions, $p$ inlets and 1 outlet

Mole balance for $S$ species

\[
\dot{n}(t) = N^T V(t) \mathbf{r}(t) + \mathbf{W}_{in} \mathbf{u}_{in}(t) - \frac{u_{out}(t)}{m(t)} n(t), \quad n(0) = n_0
\]

\[
= N^T V(t) \mathbf{r}(t) + \mathbf{C}_{in} \mathbf{q}_{in}(t) - \frac{q_{out}(t)}{V(t)} n(t)
\]

$(S \times 1)$ $(S \times R)(R \times 1)$ $(S \times p)(p \times 1)$

Mass $m$, density $\rho$, volume $V$ and concentrations $c$

\[
m(t) = 1^T_s M_w n(t), \quad \rho(t) = \phi(n(t), M_w, \rho_i), \quad V(t) = \frac{m(t)}{\rho(t)}, \quad c(t) = \frac{n(t)}{V(t)}
\]
Homogeneous reaction systems
4-way decomposition into extents

Assumption: $\text{rank} \left( \begin{bmatrix} N^T & W_{in} & n_0 \end{bmatrix} \right) = R + p + 1$

$$n \xrightarrow{\psi} \begin{bmatrix} x_r \\ x_{in} \\ \lambda \end{bmatrix} = \begin{bmatrix} S_0^T \\ M_0^T \\ q_0^T \end{bmatrix} n$$

Vessel extents of reaction $x_r$ and of flow ($x_{in}$ and $x_{out}$)

$$\dot{x}_r = S_0^T N^T V r + S_0^T W_{in} u_{in} - \frac{u_{out}}{m} x_r$$

$$x_r(0) = 0_R$$

$$\dot{x}_{in} = M_0^T N^T V r + M_0^T W_{in} u_{in} - \frac{u_{out}}{m} x_{in}$$

$$x_{in}(0) = 0_p$$

$$\dot{\lambda} = q_0^T N^T V r + q_0^T W_{in} u_{in} - \frac{u_{out}}{m} \lambda$$

$$\lambda(0) = 1$$

$$x_{out} = 1 - \lambda$$

$$x_{out}(0) = 0$$

$$x_{iv} = 0_{S-R-p}$$
Homogeneous reaction systems
4-way decomposition into extents

Assumption: \( \text{rank} \left( \begin{bmatrix} N^T & W_{in} & n_0 \end{bmatrix} \right) = R + p + 1 \)

\[ n \xrightarrow{\psi} \begin{bmatrix} x_r \\ x_{in} \\ \lambda \end{bmatrix} = \begin{bmatrix} S_0^T \\ M_0^T \\ q_0 \end{bmatrix} n \]

Vessel extents of reaction \( x_r \) and of flow \( (x_{in} \text{ and } x_{out}) \)

\[
\dot{x}_r = V \, r - \frac{u_{out}}{m} \, x_r \\
\dot{x}_{in} = u_{in} - \frac{u_{out}}{m} \, x_{in} \\
\dot{\lambda} = -\frac{u_{out}}{m} \, \lambda \\
x_{out} = 1 - \lambda
\]

\( x_r(0) = 0_R \) \quad \( x_{in}(0) = 0_p \) \quad \( \lambda(0) = 1 \) \quad \( x_{out}(0) = 0 \)

Reconstruction:

\[ n(t) = n_0 + N^T \, x_r(t) + W_{in} \, x_{in}(t) - n_0 \, x_{out}(t) \]
Homogeneous reaction systems
Reaction Variant (RV) form

When \( \text{rank} \left( \begin{bmatrix} N^T & W_{in} & n_0 \end{bmatrix} \right) < R + p + 1 \)

- Compute \( x_{in} \) and \( x_{out} \) using \( u_{in}, u_{out} \) and \( m \)

\[
\dot{x}_{in} = u_{in} - \frac{u_{out}}{m} x_{in} \quad x_{in}(0) = 0_p \\
\dot{x}_{out} = \frac{u_{out}}{m} (1 - x_{out}) \quad x_{out}(0) = 0
\]

- Compute \( n^{RV} \) (RV-form of \( n \))

\[
n^{RV}(t) = n(t) - n_0 - W_{in} x_{in}(t) + n_0 x_{out}(t) = N^T x_r(t)
\]

- Compute \( x_r \) from \( n^{RV} \)

\[
x_r(t) = N^{T^+} n^{RV}(t) = N^{T^+} (n(t) - n_0 - W_{in} x_{in}(t) + n_0 x_{out}(t))
\]
Gas-liquid reaction systems

Assumptions:

- the gas and liquid phases are homogeneous
- the reactions take place in the liquid bulk
- the mass transfer is described by the two-film theory with no accumulation in the boundary layer
Gas-liquid reaction systems
Balance equations

Mole balance in the **Liquid phase**

\[ \dot{n}_\ell(t) = N^T V_\ell(t) r(t) + W_{m,\ell} \zeta(t) + W_{in,\ell} u_{in,\ell}(t) - \frac{u_{out,\ell}(t)}{m_\ell(t)} n_\ell(t), \quad n_\ell(0) = n_{\ell 0} \]

Mole balance in the **Gas phase**

\[ \dot{n}_g(t) = - W_{m,g} \zeta(t) + W_{in,g} u_{in,g}(t) - \frac{u_{out,g}(t)}{m_g(t)} n_g(t), \quad n_g(0) = n_{g 0} \]

Mass \( m_\ell \), density \( \rho_\ell \), volumes \( V_\ell \) and \( V_g \), and concentrations \( c_\ell \)

\[
m_\ell(t) = 1_S^T M_{w,\ell} n_\ell(t), \quad V_\ell(t) = \frac{m_\ell(t)}{\rho_\ell(t)}, \quad c_\ell(t) = \frac{n_\ell(t)}{V_\ell(t)}
\]

\[
\rho_\ell(t) = \phi(c_\ell(t), M_{w,\ell}, \rho_{\ell i}) \quad V_g(t) = V_{\text{tot}} - V_\ell(t)
\]
Gas-liquid reaction systems
5-way decomposition into extents

Assumption: \( \text{rank} \left( \begin{bmatrix} N^T & W_{m,\ell} & W_{in,\ell} & n_{\ell_0} \end{bmatrix} \right) = R + p_m + p_\ell + 1 \)

Vessel extents of reaction \( x_r \) and of flow (\( x_{in} \) and \( x_{out} \))

\[
\begin{align*}
\dot{x}_r &= V_\ell r - \frac{u_{out,\ell}}{m_\ell} x_r \\
\dot{x}_m,\ell &= \zeta - \frac{u_{out,\ell}}{m} x_{m,\ell} \\
\dot{x}_{in,\ell} &= u_{in,\ell} - \frac{u_{out,\ell}}{m} x_{in,\ell} \\
\dot{\lambda}_\ell &= -\frac{u_{out,\ell}}{m_\ell} \lambda_\ell \\
x_{out,\ell} &= 1 - \lambda_\ell
\end{align*}
\]

Reconstruction: \( n_\ell (t) = n_{\ell_0} + N^T x_r (t) + W_{m,\ell} x_{m,\ell} (t) + W_{in,\ell} x_{in,\ell} (t) - n_{\ell_0} x_{out,\ell} (t) \)
Gas-liquid reaction systems
Reaction & Mass-transfer Variant (RMV) form

When \( \text{rank}\left(\begin{bmatrix} N^T & W_{m,\ell} & W_{in,\ell} & n_{\ell,0} \end{bmatrix}\right) < R + p_m + p_{\ell} + 1 \)

• Compute \( x_{in,\ell} \) and \( x_{out,\ell} \) using \( u_{in,\ell}, u_{out,\ell} \) and \( m_{\ell} \)
  \[
  \dot{x}_{in,\ell} = u_{in,\ell} - \frac{u_{out,\ell}}{m_{\ell}} x_{in,\ell} \quad x_{in,\ell}(0) = 0_{p_{\ell}}
  \]
  \[
  \dot{x}_{out,\ell} = \frac{u_{out,\ell}}{m_{\ell}} (1 - x_{out,\ell}) \quad x_{out,\ell}(0) = 0
  \]

• Compute \( n_{\ell}^{RMV} \) (RMV-form of \( n_{\ell} \))
  \[
  n_{\ell}^{RMV}(t) = n_{\ell}(t) - n_{\ell,0} - W_{in,\ell} x_{in,\ell}(t) + n_{\ell,0} x_{out,\ell}(t) = N^T x_r(t) + W_{m,\ell} x_{m,\ell}(t)
  \]

• Compute \( x_r \) and \( x_{m,\ell} \) from \( n_{\ell}^{RMV} \)
  \[
  \begin{bmatrix} x_r(t) \\ x_{m,\ell}(t) \end{bmatrix} = \left[ N^T \quad W_{m,\ell} \right]^+ n_{\ell}^{RMV}(t) = \left[ N^T \quad W_{m,\ell} \right]^+ (n_{\ell}(t) - n_{\ell,0} - W_{in,\ell} x_{in,\ell}(t) + n_{\ell,0} x_{out,\ell}(t))
  \]
Individual identification of reaction rates from the extents of reaction

Identification of the rate expression $r_i$ and estimation of the associated kinetic parameters $\theta_i$ for each $i$-th reaction by comparing the computed extents $x_{r,i}(t)$ and the simulated extents $\tilde{x}_{r,i}(t)$ of reaction

$$\dot{x}_{r,i} = \nabla_\ell(t) r_i(\theta_i, c_\ell(t)) - \frac{u_{out,\ell}(t)}{m_\ell(t)} \tilde{x}_{r,i}(t) \quad \tilde{x}_{r,i}(0) = 0$$
Incremental identification using spectroscopic data

**Homogeneous reaction systems**

Calibration step

\[ F_{\text{prog}} = \varphi(C_c, Y_c) \]

Numbers of moles

\[ \hat{n}(t) = F_{\text{prog}} a_v(t) \]

Extents using \( \hat{n} \)

\[ x_r(t) = S_0^T \hat{n}(t) \]

using \( \hat{n}^{RV} \) or \( \hat{n}_{\ell}^{RMV} \)

\[ x_r(t) = N^T \hat{n}^{RV}(t) \]

**Gas-liquid reaction systems**

Calibration step

\[ F_{\text{prog}} = \varphi(C_{\ell,c}, Y_{\ell,c}) \]

Numbers of moles

\[ \hat{n}_\ell(t) = F_{\text{prog}} a_v(t) \]

Extents using \( \hat{n}_\ell \)

\[ x_r(t) = S_{\ell 0}^T \hat{n}_\ell(t) \]

\[ x_{m,\ell}(t) = M_{m,\ell 0}^T \hat{n}_\ell(t) \]

\[ x_r(t) = N^T W_{m,\ell}^T \hat{n}_{\ell}^{RMV}(t) \]

Extents can subsequently be used for model identification

\( F_{\text{prog}} \) is the prognostic matrix \((S \times L)\) from calibration, \( a_v(t) = a(t)V_\ell(t) \) with dimension \((L \times 1)\)
Homogeneous reaction systems
Acetoacetylation of pyrrole

The acetoacetylation of Pyrrole (A) with Diketene (B) catalyzed by Pyridine (K) involves seven species \( (S = 7) \). Four reactions \( (R = 4) \) produce 2-acetoacetyl pyrrole (C), Dehydroacetic acid (D), Oligomers (E) and a By-product (F).

\[
\begin{align*}
\text{R1:} & \quad A + B \xrightleftharpoons[K]{K} C \\
\text{R2:} & \quad B + B \xrightleftharpoons[K]{K} D \\
\text{R3:} & \quad B \xrightarrow{K} E \\
\text{R4:} & \quad C + B \xrightleftharpoons[K]{K} F
\end{align*}
\]

\[
\begin{align*}
r_1 &= k_1 c_A c_B c_K \\
r_2 &= k_2 c_B^2 c_K \\
r_3 &= k_3 c_B \\
r_4 &= k_4 c_c c_B c_K
\end{align*}
\]

\[
N = \begin{bmatrix}
-1 & -1 & 1 & 0 & 0 & 0 & 0 \\
0 & -2 & 0 & 1 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 1 & 0 & 0 \\
0 & -1 & -1 & 0 & 0 & 1 & 0
\end{bmatrix}
\]

The experiment is performed in a CSTR, assuming a constant density, with one inlet \( (p = 1) \) and one outlet.
Homogeneous reaction systems
Acetoacetylation of pyrrole

Pure Component Spectra: $F_{prog} = E^+ \left( S = 7 \times L = 1000 \right)$

Calibration set (10 spectra):

$A$: Pyrrole
$B$: Diketene
$C$: 2-acetoacetyl pyrrole
$D$: Dehydroacetic acid
$E$: oligomer

$F$: By-product
$K$: Pyridine

$A_c$

$noise = N\left[ 0, 0.1\% \max(E) \right]$

$noise = N\left[ 0, 0.1\% \max(C_c) E \right]$
Homogeneous reaction systems
Acetoacetylation of pyrrole

\[ \text{rank} \left( \begin{bmatrix} N^T & C_{in} & n_0 \end{bmatrix} \right) = 6 = R + p + 1 \]

\[ a_v(t) = a(t) V(t) \]

noise = \[ N \begin{bmatrix} 0, 3\% \max(c(t)) \end{bmatrix} \]
Homogeneous reaction systems
Acetoacetylation of pyrrole

Fitting of each extent individually

<table>
<thead>
<tr>
<th></th>
<th>Simulation</th>
<th>Fitting</th>
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<tbody>
<tr>
<td></td>
<td></td>
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</tr>
<tr>
<td>R1</td>
<td>M1</td>
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<td>E</td>
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<td>E</td>
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<td></td>
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<td>PLS : M4</td>
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</tbody>
</table>

M1: $r = k c_A c_B c_K$, M2: $r = k c_B^2 c_K$, M3: $r = k c_B$, M4: $r = k c_c c_B c_K$

PCR and PLS calibrations performed with 7 factors

<table>
<thead>
<tr>
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<th>$r_1$</th>
<th>$kc_B c_K$</th>
<th>$kc_A c_K$</th>
<th>$kc_A c_B$</th>
<th>$kc_A c_B c_K$</th>
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<tr>
<td>ssq</td>
<td>2.802</td>
<td>0.114</td>
<td>0.100</td>
<td>0.064</td>
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</tbody>
</table>

Model $x_{r,1}(t)$ [mol]
Gas-liquid reaction systems
Chlorination of butanoic acid

The reaction of Butanoic acid (BA) with chlorine (Cl₂) involves seven species ($S = 7$). Two reactions ($R = 2$) produce $\alpha$-mono-chloro-butanoic acid (MBA), $\alpha$-di-chloro-butanoic acid (DBA) and Hydrochloric acid (HCl). Ethanol ($EtOH$) is used as liquid solvent and Air is initially present in the reactor.

R1: $BA + Cl_2 \xrightarrow{in \ EtOH} MBA + HCl$

$R2: BA + 2 \ Cl_2 \xrightarrow{in \ EtOH} DBA + 2 \ HCl$

$$r_1 = k_1 c_{\ell,BA} c_{\ell,Cl_2} \sqrt{c_{\ell,MBA}}$$

$$r_2 = k_2 r_1 c_{\ell,Cl_2}$$

$$N = \begin{bmatrix} -1 & -1 & 1 & 1 & 0 & 0 & 0 \\ -1 & -2 & 0 & 2 & 1 & 0 & 0 \end{bmatrix}$$

Species in the Liquid phase ($S_\ell = 6$): $BA, Cl_2, MBA, HCl, DBA$ and $EtOH$

Species in the Gas phase ($S_g = 3$): $Cl_2, HCl, (Air)$

Transferring species ($p_m = 2$): $Cl_2, HCl$
Gas-liquid reaction systems
Chlorination of butanoic acid

Liquid phase
One inlet of $BA$ ($p_\ell = 1$) and one outlet
The density changes with the composition
The outlet is regulated to maintain the mass of the liquid constant

Gas phase
One inlet of $Cl_2$ ($p_g = 1$) and one outlet
The outlet is regulated to maintain the total pressure at 10 bar

\[
\begin{bmatrix}
0 \\
0 \\
10^{-5} \\
0 \\
0 \\
100
\end{bmatrix}
= n_{\ell0}
\]

\[
\begin{bmatrix}
0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix}
= W_{m,\ell}
\]

\[
\begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & 0.095 \\
0 & 0 & 0
\end{bmatrix}
= n_{g0}
\]

\[
\begin{bmatrix}
0.0141 \\
0 \\
0
\end{bmatrix}
= W_{in,g}
\]

\[
\begin{bmatrix}
1 & 0 \\
0 & 1 \\
0 & 0
\end{bmatrix}
= W_{m,g}
\]
Gas-liquid reaction systems
Chlorination of butanoic acid

Pure Component Spectra: $F_{prog} = E^+ \left( S_a = 5 \times L = 1000 \right)$

The pure spectrum of EtOH is treated as background spectrum
Air does not absorb

Calibration set (10 spectra):
Gas-liquid reaction systems
Chlorination of butanoic acid

\[ \text{rank}(N^T W_{m,\ell} W_{in,\ell} n_{\ell0}) = 5 < R + p_m + p_\ell + 1 = 6 \times \]

\[ a_v(t) = a(t)V(t) \]

\[ \text{noise} = N[0, 3\% \max(c(t))] E \]
Gas-liquid reaction systems
Chlorination of butanoic acid

Fitting of each extent individually

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<tr>
<td>R1</td>
<td>M1</td>
</tr>
<tr>
<td>R2</td>
<td>M2</td>
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<td>PLS : M1</td>
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<tr>
<td></td>
<td>M2</td>
</tr>
<tr>
<td></td>
<td>PLS : M2</td>
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</tbody>
</table>

M1: \( r = k c_{\text{BA}} c_{\text{Cl}_2} \sqrt{c_{\text{MBA}}} \), M2: \( r = k c_{\text{BA}}^2 c_{\text{Cl}_2} \sqrt{c_{\text{MBA}}} \)

PCR and PLS calibrations performed with 5 factors

<table>
<thead>
<tr>
<th>( r_1 )</th>
<th>( k c_{\text{BA}} c_{\text{Cl}_2} )</th>
<th>( k c_{\text{BA}}^2 c_{\text{Cl}_2} )</th>
<th>( k c_{\text{Cl}_2} )</th>
<th>( k c_{\text{BA}} c_{\text{Cl}<em>2} \sqrt{c</em>{\text{MBA}}} )</th>
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Conclusions

Extent-based incremental identification
• decouples each reaction from other reactions and mass transfers
• allows investigating each reaction individually
• leads to model reduction:
  Homogeneous reaction systems: \( S \rightarrow R + p + 1 \)
  Gas-liquid reaction systems: \( S_\ell \rightarrow R + p_m + p_\ell + 1 \)

Extension to spectroscopic data with calibration
• requires computing a minimum number of concentrations (liquid phase)
  Homogeneous reaction systems: \( R \)
  Gas-liquid reaction systems: \( R + p_m \)
or requires an additional source of measurements in the liquid/gas phase

Outlook: is a calibration-free approach possible?
Thank you for your attention

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