

# INCREMENTAL MODEL IDENTIFICATION OF GAS-LIQUID REACTION SYSTEMS

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## CONTEXT

Identification of kinetic models is important for monitoring, control and optimization of industrial processes. Kinetic models are often based on first principles and expressed as conservation and constitutive equations. For a well-mixed phase  $f \in \{G,L\}$  comprising  $R_f$  reactions,  $p_m$  mass transfers (at steady state),  $p_f$  inlets and 1 outlet, the differential mole balance can be defined as:

$$\dot{\mathbf{n}}_f(t) := \Phi_f(\mathbf{k}_{r,f}, \mathbf{k}_m, t) := \mathbf{N}_f^T \mathbf{r}_{v,f}(\mathbf{k}_{r,f}, t) \pm \mathbf{W}_{m,f} \boldsymbol{\zeta}(\mathbf{k}_m, t) + \mathbf{W}_{in,f} \mathbf{u}_{in,f}(t) - \frac{u_{out,f}(t)}{m_f(t)} \mathbf{n}_f(t), \quad \mathbf{n}_f(0) = \mathbf{n}_{0,f}$$

with a  $-$  sign for the gas phase ( $f = G$ ) and a  $+$  for the liquid phase ( $f = L$ )

## METHODOLOGY

### INCREMENTAL MODEL IDENTIFICATION

Model identification is decomposed into sub-problems of lower complexity via an incremental approach. Measured numbers of moles are first transformed into extents, which are then modeled individually.

#### STEP 1: TRANSFORMATION TO EXTENTS

$$\mathbf{n}_f(t) \rightarrow \begin{bmatrix} \mathbf{x}_{r,f}(t) \\ \mathbf{x}_{m,f}(t) \\ \mathbf{x}_{in,f}(t) \\ x_{out,f}(t) \end{bmatrix} := \underbrace{\begin{bmatrix} \mathbf{N}_f^T & \pm \mathbf{W}_{m,f} & \mathbf{W}_{in,f} & \mathbf{n}_{0,f} \end{bmatrix}^+}_{\text{rank}(\cdot) = R_f + p_m + p_f + 1} (\mathbf{n}_f(t) - \mathbf{n}_{0,f})$$

This transformation reduces the dimensionality of the dynamic model and keeps only the set of states (variants) describing individually the effects of the  $R_f$  reactions,  $p_m$  mass transfers,  $p_f$  inlets and 1 outlet as  $\mathbf{x}_{r,f}$ ,  $\mathbf{x}_{m,f}$ ,  $\mathbf{x}_{in,f}$  and  $x_{out,f}$ , respectively.

$$\begin{bmatrix} \dot{\mathbf{x}}_{r,f}(t) \\ \dot{\mathbf{x}}_{m,f}(t) \\ \dot{\mathbf{x}}_{in,f}(t) \\ \dot{x}_{out,f}(t) \end{bmatrix} := \begin{bmatrix} \Phi_{r,f}(\mathbf{k}_{r,f}, t) \\ \Phi_{m,f}(\mathbf{k}_m, t) \\ \Phi_{in,f}(t) \\ \Phi_{out,f}(t) \end{bmatrix} := \begin{bmatrix} \mathbf{r}_{v,f}(\mathbf{k}_{r,f}, t) \\ \boldsymbol{\zeta}(\mathbf{k}_m, t) \\ \mathbf{u}_{in,f}(t) \\ -\frac{u_{out,f}(t)}{m_f(t)} \end{bmatrix} - \frac{u_{out,f}(t)}{m_f(t)} \begin{bmatrix} \mathbf{x}_{r,f}(t) \\ \mathbf{x}_{m,f}(t) \\ \mathbf{x}_{in,f}(t) \\ x_{out,f}(t) \end{bmatrix}, \quad \begin{bmatrix} \mathbf{x}_{r,f}(0) \\ \mathbf{x}_{m,f}(0) \\ \mathbf{x}_{in,f}(0) \\ x_{out,f}(0) \end{bmatrix} = \begin{bmatrix} \mathbf{0}_{R_f} \\ \mathbf{0}_{p_m} \\ \mathbf{0}_{p_f} \\ 0 \end{bmatrix}$$

### SIMULTANEOUS MODEL IDENTIFICATION

Identification of reaction kinetics, namely, rate expressions ( $\mathbf{r}_{v,f}$  and  $\boldsymbol{\zeta}_f$ ) and rate parameters ( $\mathbf{k}_{r,f}$  and  $\mathbf{k}_m$ ), is commonly performed in one step via a simultaneous approach, where a dynamic model comprising all kinetic steps is postulated and the corresponding parameters are estimated **simultaneously** by comparing the measured and modeled numbers of moles (least-squares minimization):

$$\min_{\mathbf{k}_{r,f}, \mathbf{k}_m} \left\| \mathbf{n}_f(t) - \hat{\mathbf{n}}_f(t) \right\|^2 \quad \text{s.t.} \quad \dot{\hat{\mathbf{n}}}_f(t) = \Phi_f(\mathbf{k}_{r,f}, \mathbf{k}_m, t)$$

The number of moles  $\mathbf{n}_f(t)$  can be reconstructed as:

$$\mathbf{n}_f(t) = \mathbf{N}_f^T \mathbf{x}_{r,f}(t) \pm \mathbf{W}_{m,f} \mathbf{x}_{m,f}(t) + \mathbf{W}_{in,f} \mathbf{x}_{in,f}(t) + \mathbf{n}_{0,f} (1 + x_{out,f}(t))$$

If the rank condition is not fulfilled, the measured numbers of moles can be transformed to Reaction Mass-transfer Variant (RMV) form using measurements of  $\mathbf{u}_{in,f}(t)$  and  $u_{out,f}(t)$ , and the extents of reaction and mass transfer are computed as:

$$\begin{bmatrix} \mathbf{x}_{r,f}(t) \\ \mathbf{x}_{m,f}(t) \end{bmatrix} = \underbrace{\begin{bmatrix} \mathbf{N}_f^T & \pm \mathbf{W}_{m,f} \end{bmatrix}^+}_{\text{rank}(\cdot) = R_f + p_m} \left( \mathbf{n}_f(t) - \underbrace{\begin{bmatrix} \mathbf{W}_{in,f} & \mathbf{n}_{0,f} \end{bmatrix}}_{\mathbf{n}_f^{RMV}(t)} \begin{bmatrix} \hat{\mathbf{x}}_{in,f}(\mathbf{u}_{in,f}, t) \\ 1 + \hat{x}_{out,f}(u_{out,f}, t) \end{bmatrix} \right)$$

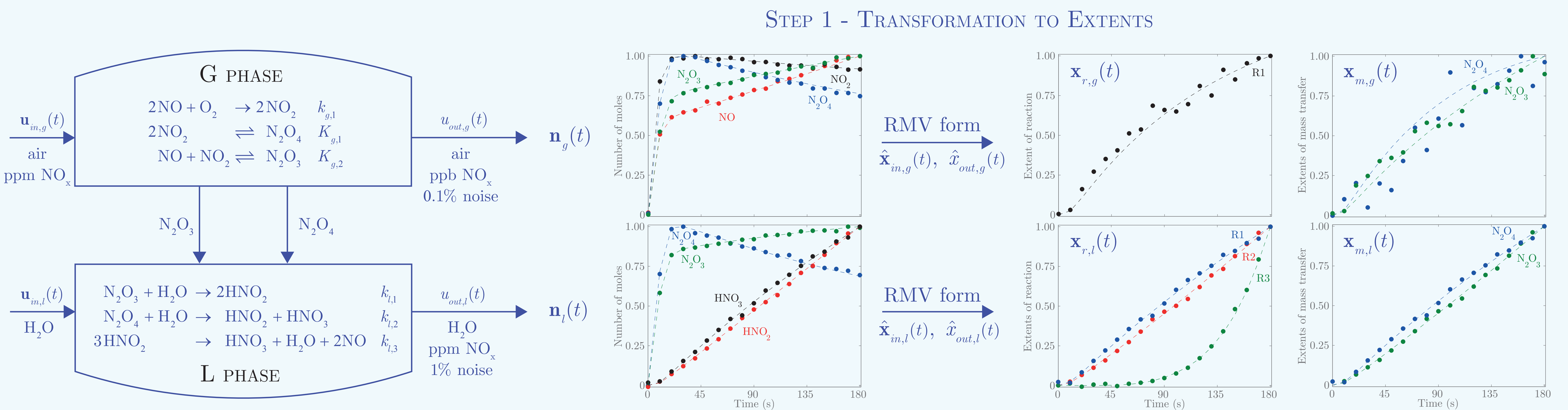
#### STEP 2: ESTIMATION OF RATE PARAMETERS

Postulated rate expressions and rate parameters are estimated **individually** by comparing one at a time the corresponding measured and modeled extents:

$$\begin{aligned} \min_{k_{r,f,i}} \left\| x_{r,f,i}(t) - \hat{x}_{r,f,i}(k_{r,f,i}, t) \right\|^2 & \quad \text{s.t.} \quad \dot{\hat{x}}_{r,f,i}(t) = \Phi_{r,f,i}(k_{r,f,i}, t), \quad \forall i = 1, \dots, R_f \\ \min_{k_{m,j}} \left\| x_{m,f,j}(t) - \hat{x}_{m,f,j}(k_{m,j}, t) \right\|^2 & \quad \text{s.t.} \quad \dot{\hat{x}}_{m,f,j}(t) = \Phi_{m,f,j}(k_{m,j}, t), \quad \forall j = 1, \dots, p_m \end{aligned}$$

## APPLICATION: FLUE GAS TREATMENT

The startup of an isothermal continuous absorber of nitrogen oxides is simulated. A constant flux of flue gas containing NO and air reacts and forms  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  in the gas phase.  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  undergo steady-state mass transfer into the liquid phase and react with water producing  $\text{HNO}_2$ ,  $\text{HNO}_3$  and NO.



#### STEP 2 - ESTIMATION OF PARAMETERS

	G PHASE	$k_{g,1}$ (kPa $^2$ ·s $^{-1}$ )	$K_{g,1}$ (M $^{-1}$ )	$K_{g,2}$ (M $^{-1}$ )	L PHASE	$k_{l,1}$ (s $^{-1}$ )	$k_{l,2}$ (s $^{-1}$ )	$k_{l,3}$ (M $^2$ ·s $^{-1}$ )
Estimated		0.0020 ± 0.0001	0.055 ± 0.003	0.0060 ± 0.0003	Estimated	1103 ± 20	17008 ± 270	0.0092 ± 0.0002
Simulated		0.0020	0.0557	0.0060	Simulated	1100	17000	0.0092

## REFERENCES

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- Bhatt et al., Ind. & Eng. Chem. Res. 50 (2011), 12960
- Srinivasan et al., Chem. Eng. J. 207-208 (2012), 785
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## PERSPECTIVES

- Analysis of systems with accumulation and reaction in the film
- Extension of the methodology to distributed reaction systems (tubular reactors)
- Modeling of integrated reaction-separation systems (e.g. reactive distillation)

