Incremental model identification of gas-liquid reaction systems

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Identification of kinetic models is an important task for monitoring, control and optimization of industrial processes. Kinetic models are often based on first principles, which describe the evolution of the states – numbers of moles, temperature and volume – by means of conservation and constitutive equations. Identification of reaction kinetics, namely, rate expressions and rate parameters, represents the main challenge in constructing first-principles models. Estimation of parameters is especially difficult for fluid-fluid reaction systems when chemical species transfer between phases and possibly react in the bulk of the two phases.

The identification task is commonly performed in one step via a simultaneous method. In this approach, a dynamic model comprising all kinetic steps, whether physical or chemical, is postulated, and the corresponding model parameters are estimated by comparing measured and modeled concentrations. The procedure is repeated for all combinations of model candidates, and the combination with the best fit is selected. However, simultaneous identification can be computationally costly when many candidate rate laws are available. Furthermore, this method often leads to high parameter correlation, and thus any structural mismatch in the modeling of one part of the model leads to errors in all estimated parameters.

Alternatively, model identification can be carried out over several steps via an incremental method. This way, the identification task is decomposed into sub-problems of lower complexity. Measured concentrations are transformed into extents, which can then be modeled individually [1-3]. This transformation reduces the dimensionality of the dynamic model since all redundant states (invariants) can be removed. More importantly, the remaining states (variants) represent the minimal set of states describing, individually, the effects of reaction, mass transfer and transport, inlets and outlets. Postulated rate expressions (and rate parameters) are validated and estimated – one at a time – by comparing the corresponding measured and modeled extents. This approach reduces significantly the computational effort and convergence problems. Since each kinetic step can be dealt with individually, there is no correlation between the parameters of the different physical and chemical phenomena.

This presentation will briefly review the extent-based model identification and then illustrate it with the absorption of nitrous oxides in water, which represents an important step in the treatment of flue gas and constitutes a complex reaction system with multiple reactions in both the gas and liquid phases.

[1] Bhatt et al., *Incremental Identification of Reaction and Mass-Transfer Kinetics Using the Concept of Extents*, Ind. & Eng. Chem. Res. 50, 12960-12974, **2011**
[2] Srinivasan et al., *Extent-based Incremental Identification of Reaction Systems Using Concentration and Calorimetric Measurements*, Chem. Eng. J. 208, 785-793, **2012**
[3] Billeter et al., *Extent-based Kinetic Identification using Spectroscopic Measurements and Multivariate Calibration*, Anal. Chim. Acta 767, 21-34, **2013**