INCREMENTAL KINETIC MODELING OF SPECTROSCOPIC DATA USING A REDUCED CALIBRATION MODEL

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The identification of kinetic models is an important step for the monitoring, control and optimization of chemical processes. Kinetic models are often based on first principles that describe the evolution of concentrations by means of conservation and constitutive equations. Identification of reaction kinetics, namely, rate expressions and rate parameters, represents the main challenge in constructing such first-principles models.

Absorption spectroscopy is the method of choice for monitoring the kinetics of reaction systems. Calibration methods, such as PCR or PLS, are commonly used to convert absorbance to indirect concentrations measurements. To avoid the difficult and long task of building a calibration for all species, one often designs a reduced calibration model involving only a subset of important species.

Incremental kinetic modeling is a method that decomposes the original identification problem into sub-problems of lower complexity. In its extent-based variant, the concentrations are first transformed to extents, and the resulting extents are then modeled individually [1]. However, a strong condition for using this incremental method is that rank($\mathbf{B}$) = R, where $\mathbf{B}$ is the matrix of structural information (stoichiometry and inlet concentrations) and R is the number of independent reactions. This rank condition implies that the number of measured (calibrated) concentrations (S_a) be greater than or equal to R, namely, $S_a \geq R$ [2].

In this contribution, we relax this constraint and consider the case $S_a < R$. To date, two approaches exist to adapt the extent-based kinetic modeling to this situation. The first approach consists in the dynamic modeling of ($R - S_a$) extents of reaction using candidate rate expressions and simultaneous estimation of their rate parameters (minimizing the difference between the S_a simulated and measured concentrations), followed by the algebraic computation of the S_a remaining extents of reaction and the incremental identification of their corresponding rate expressions [3]. The second approach consists in expressing the effect of the R reactions on the concentrations of the calibrated species by means of $S_a < R$ extents of reactions, and identifying via a procedure based on graph theory the smallest subsets of reactions whose rate parameters can be estimated separately [4].

This contribution briefly reviews these two approaches for the case $S_a < R$ and illustrates them via a reaction system monitored by spectroscopy.

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