A First Course on Kinetics and Reaction Engineering

How To Test a Rate Expression Using Differential Data Analysis*

1. If the data were obtained using a PFR, make sure the conversion was small (less than ca. 5%) in all experiments
2. Write the mole balance design equation (batch or PFR, as appropriate) for any one reactant or product, substituting the mathematical function to be tested as a rate expression
3. If necessary, linearize the equation from step 1 treating the derivative as if it is an experimentally measured variable
   a. The slope(s) and intercept in the linearized equation should only depend upon quantities that have the same value for every experimental data point
   b. for a batch reactor, the rate should be evaluated at the prevailing conditions of the data point for which the derivative was estimated
   c. for a PFR, the rate should be evaluated at the average of the inlet and outlet compositions
4. Approximate the value of the derivative that appears in the design equation for each experimental data point
   a. for a batch reactor this can be done using the graphical tangent method, the polynomial method or finite differences
   b. for a PFR, this should be done using forward differences
5. For each data point, calculate the value of the dependent variable and the independent variable(s) in the linearized form of the design equation.
6. Fit the equation from step 2 or step 3 to the experimental data using linear least squares
   a. obtain best values for each slope and, if present, the intercept
   b. obtain estimates for the uncertainty in the slope(s) and, if present, the intercept
   c. obtain a correlation coefficient
   d. obtain or generate a model plot or a parity plot and residuals plots
7. Decide whether the function is sufficiently accurate in representing the data
   a. based on a correlation coefficient value close to 1.0
   b. based upon small deviations of the experimental data from the model prediction in the model plot or from the diagonal of the parity plot
   c. based upon random, non-systematic deviations of the experimental data from the model prediction in the model plot or the residuals plots
8. If the fit is sufficiently accurate, use the resulting slope(s) and intercept, and their uncertainties, to calculate the best values of the parameters that appear in the rate expression being tested, along with their uncertainties
9. If the fit is not sufficiently accurate, guess a different function and repeat from step 1

* Assuming only one reaction is taking place and the reactor model can be written in the form of a linear equation