

THE ESTIMATION PROCEEDURE

Kinetic rate constants and rate expressions can be determined from reactor data. In a batch reactor one might have measured the concentration of one or more components at different times. If you will, this is concentration versus the independent variable, time. In a PFR the data could be in the form of effluent concentration versus residence time and temperature. In a CSTR the data are likely to be composition versus residence time.

To determine the rate expression and the rate coefficients we can fit the data to the appropriate material balance. The unknown is then found by matching the model prediction against the data. When a single reaction is present, one can solve the material balance to get an analytical relation that relates concentration to the system variables. For the batch reactor example worked below this leads to

$$c_j = f(t, k, \text{ reaction order}, V_r, \text{initial conditions}, \text{stoichiometry}) \quad (1)$$

If you know all variables on the righthand side, you could simply compute the value of c_j at any time, t . Since we do not know k and/or the reaction order, we must guess them until the computed values for c_j best match the measured values. We will use an optimization algorithm, such as `fminsearch` in Matlab to minimize the error in the objective function

$$\Phi = \sum_{i=1}^n [c_j(t_i) - \hat{c}_j(t_i)]^2$$

where n is the number of data points and $\hat{c}_j(t_i)$ is the experimental measurement of c_j at time t_i . The optimization routine will search for parameter or parameters that best fit $c_j(t_i)$ to $\hat{c}_j(t_i)$. This is illustrated with the following example.

EXAMPLE

The following reaction was studied in an isothermal batch reactor.



The reaction rate is known to be first order in the concentration of acetone and first order in the concentration of HCN. When the reaction was conducted in an aqueous solution and the initial concentrations were $c_{\text{HCN},o} = 0.0758$ and $c_{\text{acetone},o} = 0.1164$ gmoles/liter, the concentration data listed in the table were recorded. Use these data to determine the magnitude of the reaction rate constant.

Time(min)	HCN concentration (gmole/liter)
73.23	0.0710
172.5	0.0655
265.4	0.0610
346.7	0.0571

For this particular problem we integrate the design equation

$$\frac{dc_{\text{HCN}}}{dt} = R_{\text{HCN}} = -kc_{\text{HCN}}(\gamma + c_{\text{HCN}})$$

where $\gamma = c_{\text{acetone,o}} - c_{\text{HCN,o}}$. After integration between time $t = 0$ and t and between $c_{\text{HCN,o}}$ and c_{HCN} , and sorting for c_{HCN} , we get

$$c_{\text{HCN}} = \frac{c_{\text{HCN,o}}\gamma}{\gamma \exp^{kt\gamma} + c_{\text{HCN,o}} \exp^{kt\gamma} - c_{\text{HCN,o}}} \quad (2)$$

The equation above represents a specific example Equation 1 of what one would get for any batch reactor, which is

Equation 2 can be used to calculate the $c_j(t_i)$ in Φ . The Matlab program `parameter_estimation.m` shows one way to solve this problem. Fitting these data to a first order rate expression results in $k = 0.0076 \text{ min}^{-1}$.