This lecture covers: Experimental methods for the determination of kinetic parameters of chemical and enzymatic reactions; determination of cell growth parameters; statistical analysis and model discrimination

Continuing the stability and multiple steady-state discussion from Lecture 11:

\[
\begin{align*}
\begin{bmatrix}
\frac{d\xi_1}{dt} \\
\frac{d\xi_2}{dt} \\
\frac{dT}{dt}
\end{bmatrix}_{SS} &= \zeta_{SS} \\
\frac{d\xi_1}{dt} &= 0 \\
\frac{d\xi_2}{dt} &= 0 \\
\frac{dT}{dt} &= 0
\end{align*}
\]

Figure 1. Three steady-state conditions shown on a G(T) versus T graph.

\[
\begin{align*}
\left\{ \begin{array}{c}
\frac{d\xi_1}{dt} = f_1(\xi_1, \xi_2, T) \\
\frac{d\xi_2}{dt} = f_2(\xi_1, \xi_2, T) \\
\frac{dT}{dt} = f_3(\xi_1, \xi_2, T)
\end{array} \right. \rightarrow \frac{d\zeta}{dt} = F(\zeta)
\end{align*}
\]

stability: we want any perturbation \( \delta\zeta \) from \( \zeta_{SS} \) to be self correcting

Cite as: William Green, Jr., course materials for 10.37 Chemical and Biological Reaction Engineering, Spring 2007. MIT OpenCourseWare (http://ocw.mit.edu), Massachusetts Institute of Technology. Downloaded on [DD Month YYYY].
i.e. \( \frac{d}{dt}(\delta z) = (-ve)\delta z \)

\[ \delta z \]

what does perturbation cause?
- back to steady-state or off elsewhere?

**Figure 2.** A small perturbation moves the system away from steady state. Does the system move back or does it move to elsewhere?

\[
\frac{dz}{dt} = F(z)
\]

\[
z = z_{ss} + \delta z
\]

\[\delta z = z - z_{ss}\]

\[
\frac{d}{dt}(\delta z) = \frac{dz}{dt} = F(\delta z + z_{ss})
\]

\[\approx \frac{dF}{dz} \delta z + F(z_{ss}) + O(\delta z^2)\]

Jacobian matrix

\[
\frac{d}{dt}(\delta z) = \sum \left( \frac{dF}{dz_m} \right)_{z_{ss}} \delta z_m
\]

\[= J \delta z
\]

\[
J = \begin{pmatrix}
\frac{df_1}{d\xi_1} & \frac{df_1}{d\xi_1} & \frac{df_1}{dT} \\
\frac{df_2}{d\xi_2} & \frac{df_2}{d\xi_2} & \frac{df_2}{dT} \\
\frac{df_3}{d\xi_1} & \frac{df_3}{d\xi_2} & \frac{df_3}{dT}
\end{pmatrix}
\]

Jacobian matrix

\[
\frac{d}{dt}(\delta z) = M(\delta z)
\]

if eigenvalues of M<0 then stable
$CO + H_2O \rightleftharpoons CO_2 + H_2 + Q$

toxic

Figure 3. Conversion (X) versus Temperature (T).

Data Collection:
- determining rate laws

Reactants $\rightarrow$ Reactor $\rightarrow$ Products, Unreacted Stuff, Byproducts

Figure 4. Schematic of a general reactor.

Product concentration versus reactant concentration $A$.

$\frac{r(conc,T)}{output-input} = \frac{[A]}{0}$

Figure 5. Product concentration versus reactant concentration $A$. 
\[ \int r \, dx \, dy \, dz \rightarrow rV \] if homogeneous

"well-stirred" reactor
(slow reactions)

"no" conversion
(really \( \sim 0.1\% \) conversion)
\[ C = C_0 \pm 1\% \rightarrow \text{can measure (output-input)} \]
\[ (r \text{ barely changes}) \]
*need very sensitive product detection

"differential reactor"

From data:

guess mechanism

vary \((k, k_{eq})\) → make a fit

1) Is mechanism \textbf{consistent} (error bars?) w/ data?
2) How to regress \(k\)? (least squares method)