10.37 Chemical and Biological Reaction Engineering, Spring 2007
Prof. William H. Green

Lecture 12: Data collection and analysis

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:

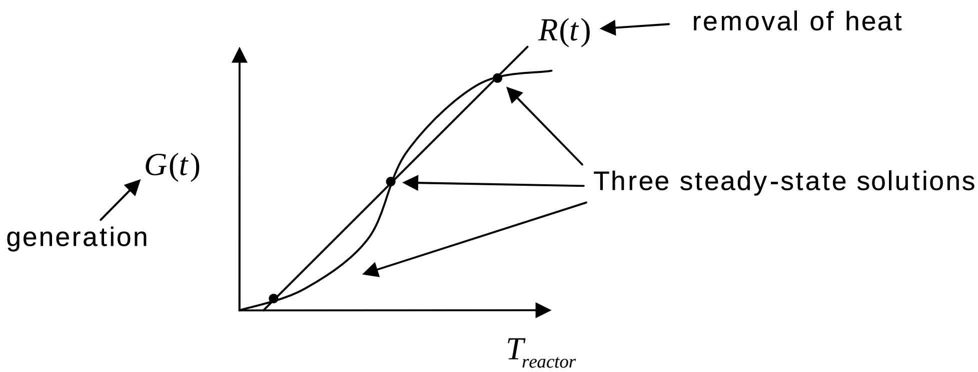


Figure 1. Three steady-state conditions shown on a G(T) versus T graph.

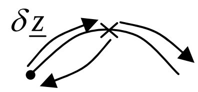
$$\begin{pmatrix} \xi_1 \\ \xi_2 \\ T \end{pmatrix}_{SS} = \underline{z}_{SS}$$

$$\frac{d\xi_1}{dt} = 0$$
$$\frac{d\xi_2}{dt} = 0 \quad \longrightarrow \text{steady-state}$$
$$\frac{dT}{dt} = 0$$

original eqns.
$$\left\{ \begin{aligned} \frac{d\xi_1}{dt} &= f_1(\xi_1, \xi_2, T) \\ \frac{d\xi_2}{dt} &= f_2(\xi_1, \xi_2, T) \\ \frac{dT}{dt} &= f_3(\xi_1, \xi_2, T) \end{aligned} \right\} \rightarrow \frac{d\underline{z}}{dt} = \underline{F}(\underline{z}) \quad \longrightarrow \text{vector notation}$$

stability: we want any perturbation $\delta\underline{z}$ from $\underline{z}_{SS}$ to be self correcting

$$\text{i.e. } \frac{d}{dt}(\delta \underline{z}) = (-ve)\delta \underline{z}$$



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?

$$\frac{d\underline{z}}{dt} = \underline{F}(\underline{z})$$

$$\underline{z} = \underline{z}_{SS} + \delta \underline{z} \qquad \delta \underline{z} = \underline{z} - \underline{z}_{SS} \leftarrow \#$$

$$\frac{d}{dt}(\delta \underline{z}) = \frac{d\underline{z}}{dt} = \underline{F}(\delta \underline{z} + \underline{z}_{SS})$$

$$\approx \boxed{\frac{d\underline{F}}{d\underline{z}}} \delta \underline{z} + \cancelto{0}{\underline{F}(\underline{z}_{SS})} + \cancelto{0}{O(\delta \underline{z}^2)}$$

Jacobian matrix

$$\frac{d}{dt}(\delta \underline{z}) = \sum \left(\frac{dF_n}{dz_m} \right)_{\underline{z}_{SS}} \delta z_m$$

$$= J \, \delta \underline{z}$$

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

Jacobian

Matrix

$$\frac{d}{dt}(\delta \underline{z}) = M \, (\delta \underline{z})$$

if eigenvalues of M<0 then stable

$$CO + H_2O \rightleftarrows CO_2 + H_2 + Q$$

toxic (CO) heat (Q)

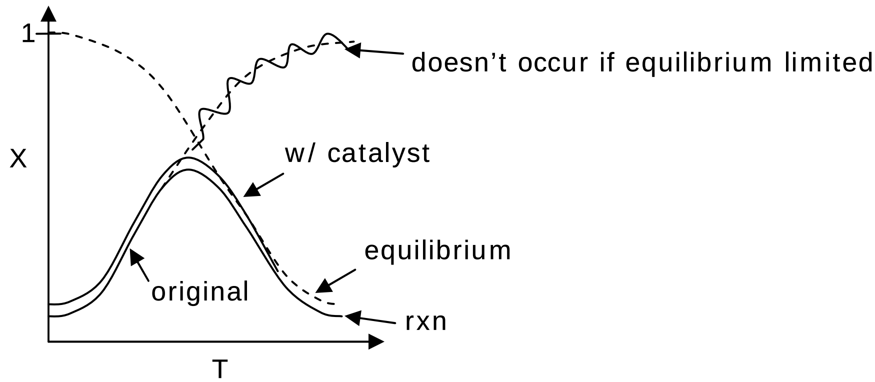


Figure 3. Conversion (X) versus Temperature (T).

Data Collection:

- determining rate laws

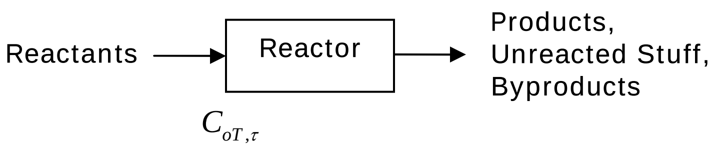
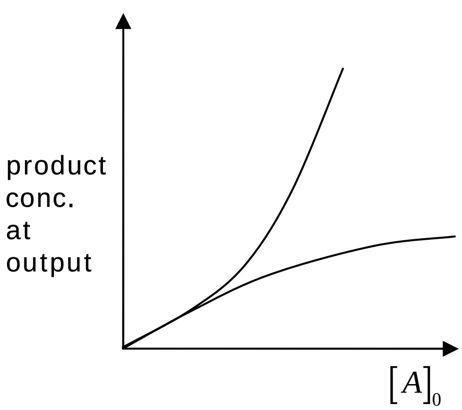


Figure 4. Schematic of a general reactor.



make plots
- get empirical expression
  → fit curve

Figure 5. Product concentration versus reactant concentration A.

r(conc,T)
ouput-input

$\int r \underbrace{dxdydz}_{dV} \rightarrow rV$ if homogeneous

"well-stirred" reactor
(slow reactions)

"no" conversion
(really ~.1% conversion)
$\underline{C} = \underline{C}_0 \pm .1\%$ → can measure (output-input)
(r barely changes)
*need very sensitive product detection
"differential reactor"

From data:

guess mechanism
vary ($\underline{k}$, $\underline{k}_{eq}$)→make a fit

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