LECTURE SIX: Stability of Steady States

This lecture covers Derivation of energy balances for ideal reactors; equilibrium conversion, adiabatic and non-adiabatic reactor operation, Experimental methods for the determination of kinetic parameters of chemical and enzymatic reactions; determination of cell growth parameters; statistical analysis and model discrimination

1. **Non-isothermal Reactors, equilibrium limitations, and stability**

Non-isothermal Reactors

$$\frac{dN_i}{dt} = \sum_{m=1}^{N\ streams} F_{i,m} + V_{cv} \sum_{l=1}^{N\ rxns} \underset{\uparrow}{\upsilon_{i,l}} r_l$$

stoichiometric coefficient

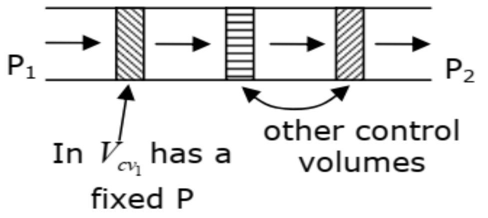
r_l - depends on concentration
- T
- catalyst

$$\underbrace{\frac{dU_{cv}^{total}}{dx}}_{\text{extensive work}} + \underbrace{P\frac{dV_{cv}}{dt}}_{\text{expansion work}} = \sum_{m=1}^{N\ streams} \underbrace{H_m^{conc}(T_m)}_{\text{intensive}} F_m^{total} + \underbrace{\dot{Q}}_{\text{heat}} + \underbrace{\dot{W}_s}_{\text{shaft work}} + (\text{other energy terms})$$

flow work

do work → $\dot{W}_s$ negative

If small control volume, pressure constant.



$P_1 \neq P_2$

Figure 1. Schematic of a PFR with small control volumes, each with a fixed P.

PFR has many small control volumes, each with its own constant P.

For isothermal
- $\dot{Q}$ adjusted to keep T constant
- Practical – have big cooling bath
- or just operate at a particular temperature found after reactor built
  - ⇒ not a good strategy, for design we want to know ahead of time
- before assumed uniform T, actually have hot spots

Where is T? In U_{cv}^{total} and $r_l(T)$.

$$\frac{dU_{cv}^{total}}{dt} = \frac{dU_{cv}^{total}}{dT}\frac{dT}{dt} + \sum_{i=1}^{N\ streams}\left(\frac{dU_{cv}^{total}}{dN_i}\right)\frac{dN_i}{dt}$$

heat capacity of system

intensive contribution of each species

substitute for $\frac{dN_i}{dt}$

Want $\frac{dY}{dt} = F(Y)$

Assume ideal mixtures

$$U_{cv}^{total} \approx \sum N_i U_i(T_{cv})$$

extensive

intensive

$$\frac{dU_{cv}^{total}}{dN_i} = U_i(T_{cv})$$

If P=Constant (Isobaric)

$$\frac{dH^{total}}{dt} = \frac{d(U+PV)}{dt} = \frac{dU}{dt} + \underbrace{\frac{dP}{dt}}_{0}V + P\frac{dV}{dt}$$

$$\underbrace{\frac{dU_{cv}^{total}}{dt} + P\frac{dV_{cv}}{dt}}_{\substack{\downarrow \\ \frac{dH^{total}}{dt}}}$$

Assume isobaric, all ideal mixtures, neglecting K.E., P.E., other energies

$$\left(\sum_{i}^{N\ species} N_i C_{p,i}\right)\frac{dT_{cv}}{dt} = \sum_{m}^{N\ streams}\sum_{i}^{N\ species} F_{i,m}\left(H_i(T_m) - H_i(T_{cv})\right)$$

$$- \sum_{i}^{N\ streams}\sum_{l}^{N\ rxns} H_i(T_{cv})V_{cv}\upsilon_{i,l}r_l(T_{cv}) + \dot{Q} + \dot{W}_s$$

stoichiometric coefficient

$$\sum_i \upsilon_{i,l}H_i(T_{cv}) \equiv \underset{l}{\Delta H_{rxn}}(T_{cv})$$

$$-\sum_{i}^{N\ streams}\sum_{l}^{N\ rxns} H_i(T_{cv})V_{cv}\upsilon_{i,l}r_l(T_{cv}) = -\sum_{l} V_{cv}r_l(T_{cv})\Delta \underset{l}{H}_{rxn}(T_{cv})$$

Assume

$$\dot{Q} \cong \underset{\substack{\uparrow \\ \text{heat} \\ \text{transfer} \\ \text{coefficient}}}{U}\underset{\substack{\uparrow \\ \text{area of} \\ \text{contact}}}{A}(\underset{\substack{\uparrow \\ \text{coolant}}}{T_a} - \underset{\substack{\uparrow \\ \text{reactor}}}{T_{cv}}) \qquad \text{(conduction)}$$

$\dot{W}_s \approx 0$ (As a stirrer, heat negligible)

If designing engines $\dot{W}_s \neq 0$.

Now just put into MATLAB and solve

Chapter 8 in Fogler
- lots of special case equations
- be careful of assumptions

Special case: Start up CSTR to a steady state
want to know ultimate T

$$\frac{dT_{cv}}{dt} = 0 \cong \sum_{m}^{N\ streams}\sum_{i}^{N\ species} F_{i,m}\left(H_i(T_m) - H_i(T_{cv})\right) - \underbrace{\sum V_{cv} r_l \Delta \underset{l}{H}_{rxn}}_{\text{All depend on } T_{CV}} + UA(T_a - T_{cv})$$

When we reach steady state, no more accumulation

$F_{A,\,in} - F_{A,\,out} + r_A V = 0$ at steady-state

See Fogler: 8.2.3

If just one reaction, one input stream, one output stream, and the system is at steady-state:

$$X_A = \frac{UA(T - T_a) + \sum F_{i,\,input}C_{p,\,i}(T - T_{in})}{F_{Ao}(-\Delta H_{rxn})}$$

In this special case, conversion and T linear
1 reaction making heat as product is made.
When $\Delta H_{rxn} =$ (-) Exothermic, reactor is hotter than cooling reactor (heat transfer important)
(+) Endothermic, reactor must be heated so that reaction will run

$$G(T) \equiv (-\Delta H_{rxn})(-r_A V/F_{Ao}) \qquad \text{Generation}$$

$$R(T) = \left(\sum \frac{F_{i,\,in}}{F_{Ao}} C_{p,\,i}\right)\left(1 + \underbrace{\frac{UA}{\sum F_{i,\,in} C_{p,\,i}}}_{K}\right)(T - T_c)$$

Heat removal

$K = 0$ Adiabatic
$K =$ Big Cooling

$$T_c = \frac{KT_a + T_{in}}{1 + K}$$

$R(T)$ linear with T

$G(T) \rightarrow$ constant at high T
- not linear with T

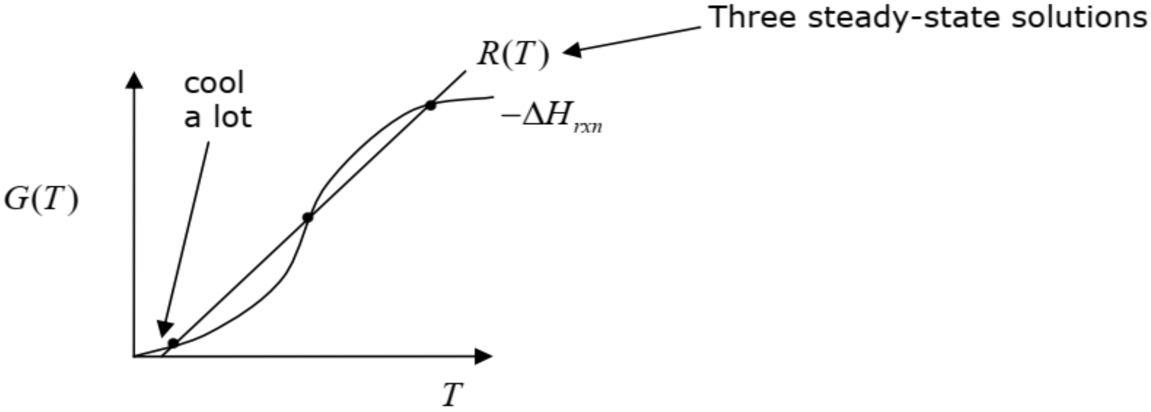


Figure 2. Graph of G(T) versus T. Three steady-state points are shown where R(T) intersects with the heat of reaction.

With multiple steady states must consider stability.

2. **Data collection and analysis**

Continuing the stability and multiple steady-state discussion

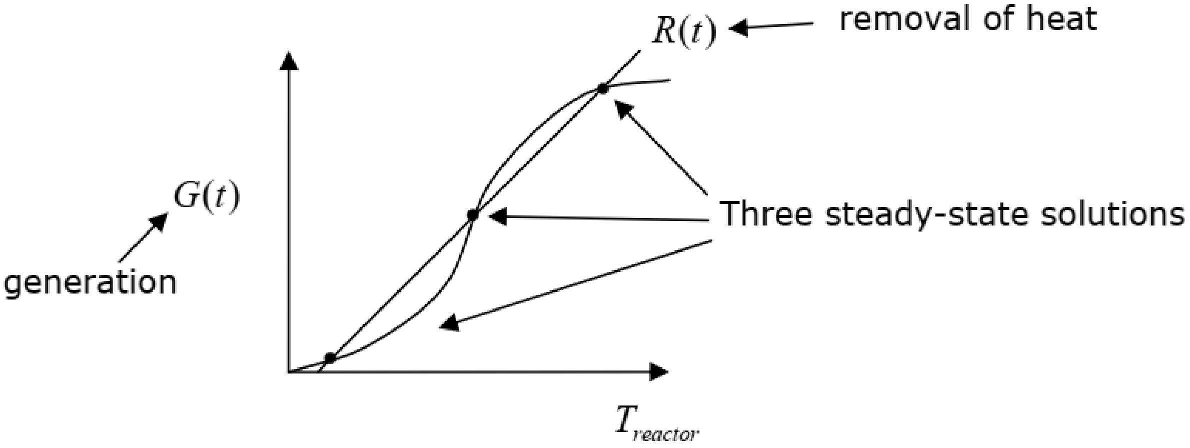


Figure 1. Three steady-state conditions shown on a G(T) versus T graph.

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

$$\left.\begin{array}{l} \dfrac{d\xi_1}{dt} = 0 \\ \dfrac{d\xi_2}{dt} = 0 \\ \dfrac{dT}{dt} = 0 \end{array}\right. \quad \longrightarrow \quad \text{steady-state}$$

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

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

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

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

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

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

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

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

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

$$\frac{d}{dt}(\delta\underline{z}) = \overset{\text{Matrix}}{M}\ (\delta\underline{z})$$

if eigenvalues of $M<0$ then stable

$$\underset{\substack{\uparrow\\ \text{toxic}}}{CO} + H_2O \rightleftarrows CO_2 + H_2 + \underset{\substack{\uparrow\\ \text{heat}}}{Q}$$

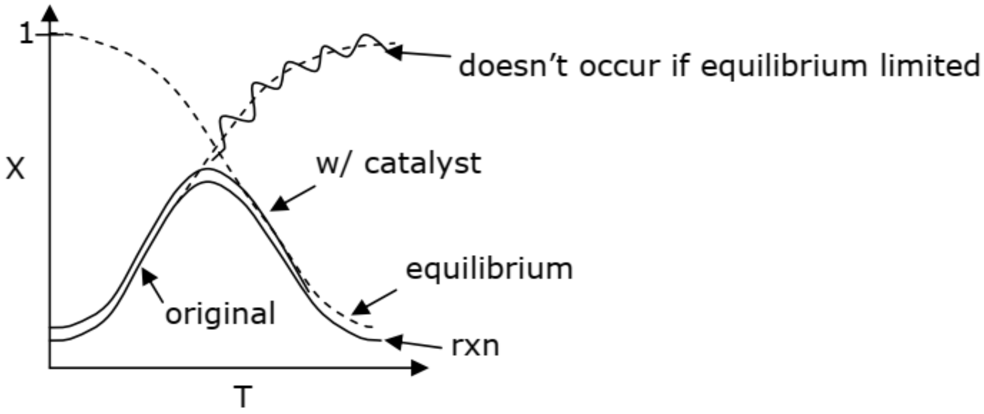


Figure 3. Conversion (X) versus Temperature (T).

Data Collection:

- determining rate laws

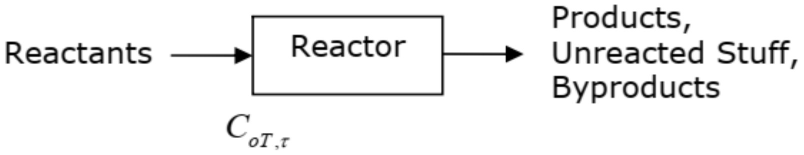
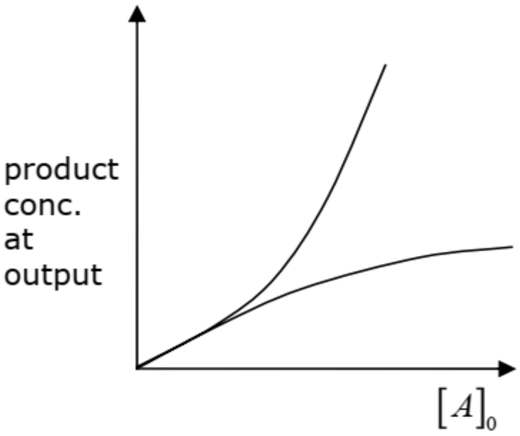


Figure 4. Schematic of a general reactor.



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 <u>consistent</u> (error bars?) w/ data?
2) How to regress $\underline{k}$? (least squares method)