ChE 344
Reaction Engineering and Design

Lecture 17: Tues, Mar 15, 2022

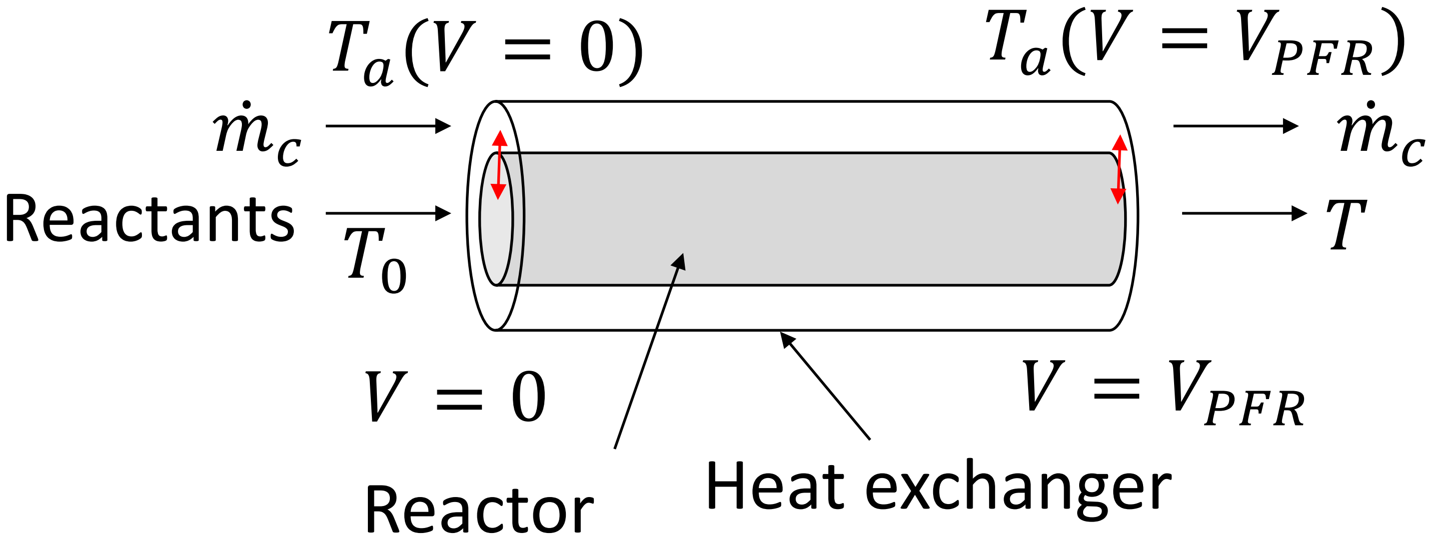
9:30am-11:00am

Multiple steady states & multiple non-isothermal reactions

Reading for today's Lecture: Chapter 12.4-12.6

Reading for Lecture 18: Chapter 12.3, 12.6

Last Lecture: Heat exchanger's energy balance along with reactor energy balance (for PFR)



$T_a(V = 0)$

$T_a(V = V_{PFR})$

$\dot{m}_c$

$\dot{m}_c$

Reactants

T_0

T

$V = 0$

$V = V_{PFR}$

Reactor

Heat exchanger

$$\frac{dT}{dV} = \frac{r_A \Delta H_{rxn} - Ua(T - T_a)}{\sum F_i C_{P,i}} \qquad \frac{-Ua(T_a - T)}{\dot{m}_c C_{P,c}} = \frac{dT_a}{dV}$$

$$F_{A0}\frac{dX}{dV} = -r_A$$

Discuss with your neighbors:

PFR: A → B, zero-order in A, endothermic and $C_{P,A} = C_{P,B}$:

What is the order of the conversions from low to high?

a. Isothermal reactor at T_0

b. Adiabatic reactor at inlet T_0

c. Reactor with heat exchanger with fluid at $T_a = T_0$

d. Reactor with heat exchanger with fluid at $T_a = T_0$ at inlet, but heat exchanger fluid cools as it passes along reactor

[✓ A) $X_{\text{isothermal}} > X_{\text{H.E.,Ta}} > X_{\text{heat exchanger,Ta(V)}} > X_{\text{adiabatic}}$]

B) $X_{\text{isothermal}} > X_{\text{heat exchanger,Ta(V)}} > X_{\text{H.E.,Ta}} > X_{\text{adiabatic}}$

C) $X_{\text{isothermal}} > X_{\text{H.E.,Ta}} = X_{\text{heat exchanger,Ta(V)}} > X_{\text{adiabatic}}$

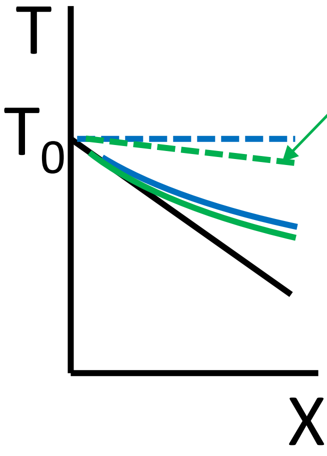
D) $X_{\text{isothermal}} > X_{\text{H.E.,Ta}} > X_{\text{heat exchanger,Ta(V)}} = X_{\text{adiabatic}}$

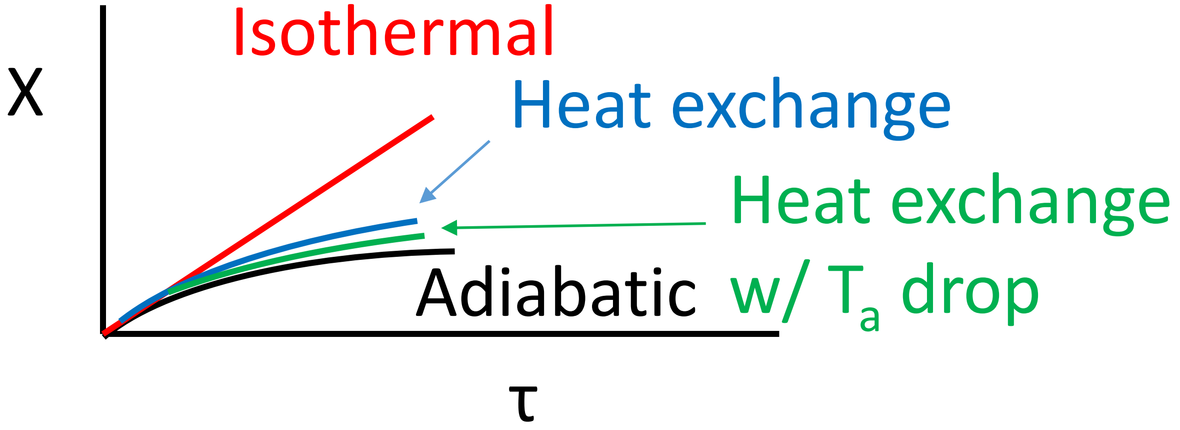
PFR: A → B, zero-order in A, endothermic and $C_{P,A} = C_{P,B}$:

Sketch X as a function of space time, assuming:

d. Reactor with heat exchanger with fluid at $T_a = T_0$ at inlet, but heat exchanger fluid cools as it passes along reactor

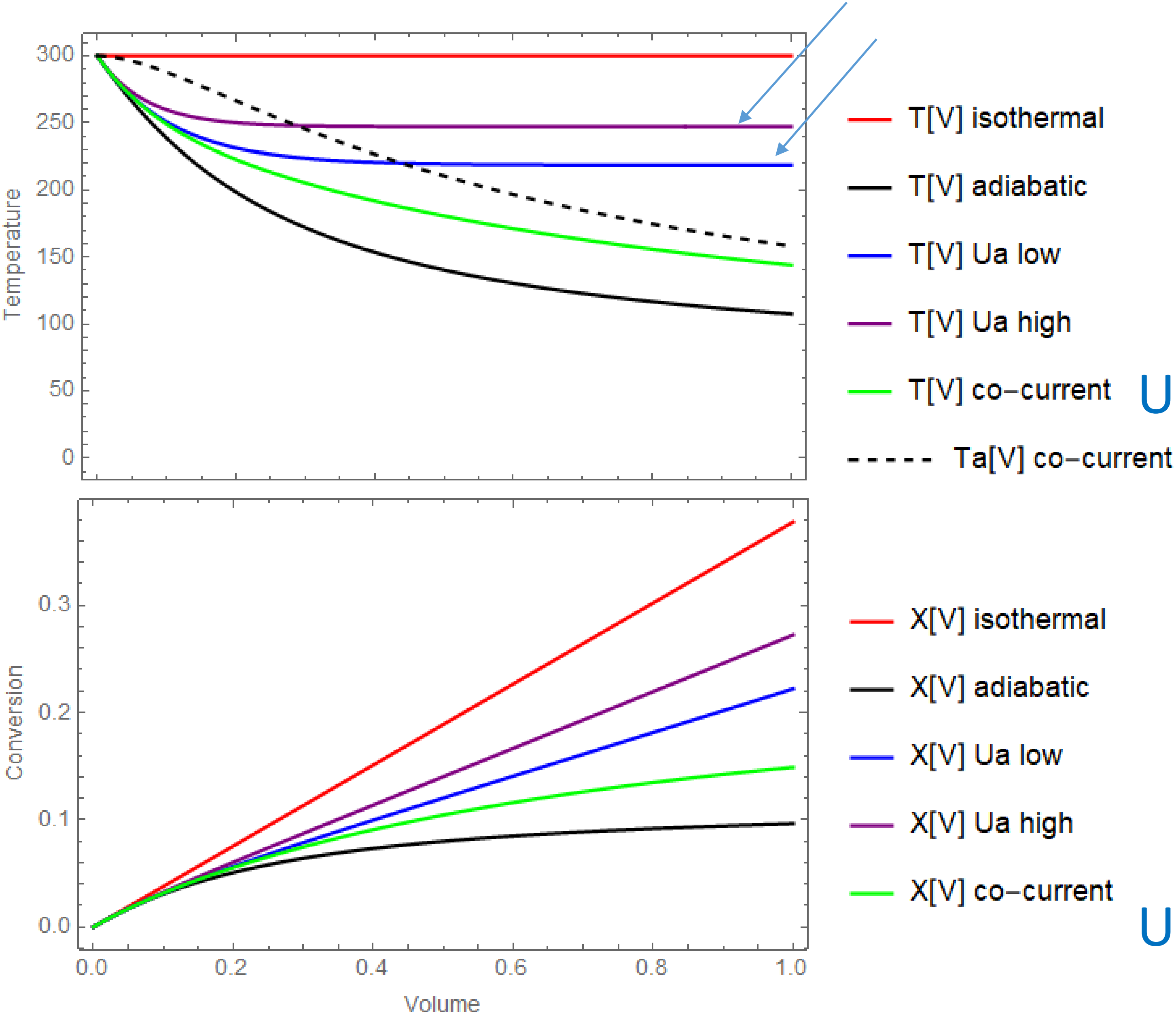
$$\frac{-Ua(T_a - T)}{\dot{m}_c C_{P,c}} = \frac{dT_a}{dV}$$





If $\dot{m}_c C_{P,c}$ is moderate:

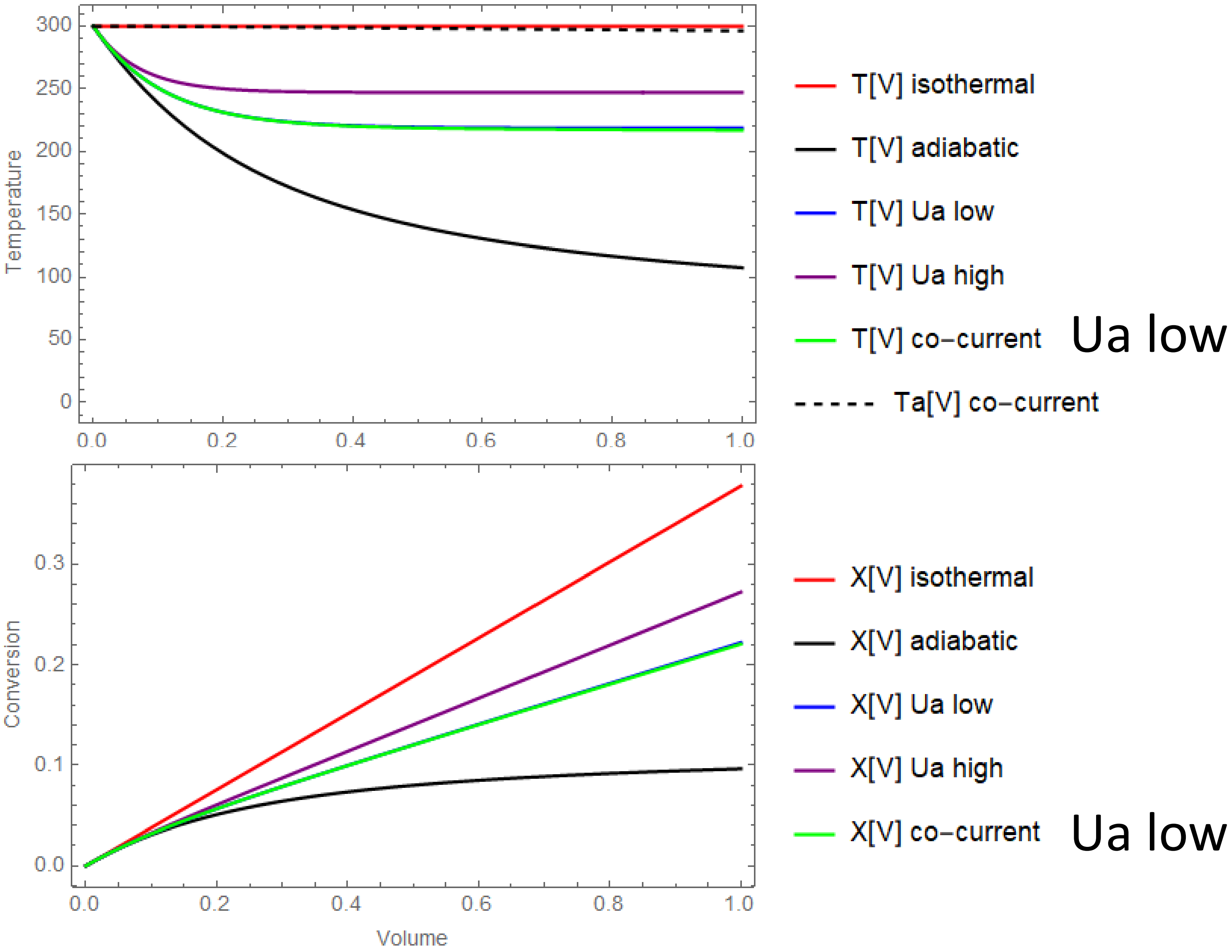
Once (T_a-T) is large enough heat removal = gen.!



Ua low

Ua low

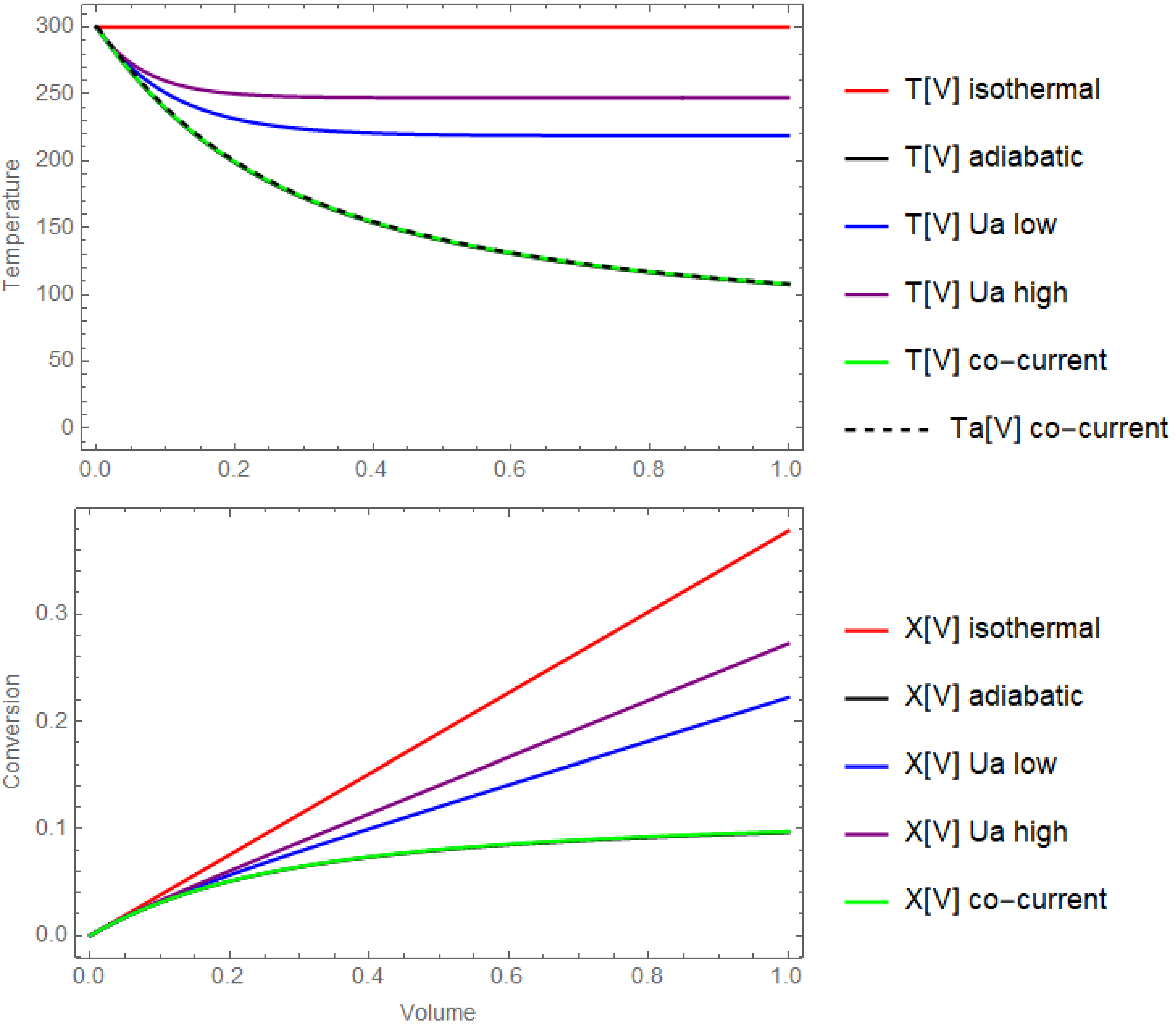
If $\dot{m}_c C_{P,c}$ is very large, T_a remains constant



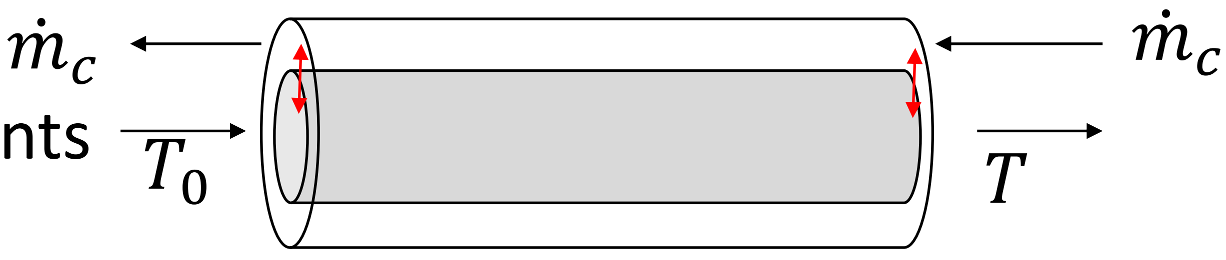
Ua low

Ua low

If $\dot{m}_c C_{P,c}$ is very small, similar to adiabatic



Countercurrent:



From EB T_{a2} → $T_a(V=0)$

$T_a(V=V_{PFR})$ ← Controlled by us T_{a0}

$\dot{m}_c$ ←

← $\dot{m}_c$

Reactants → T_0

→ T

$V=0$

$V=V_{PFR}$

Energy balance on heating fluid for countercurrent:

$$\frac{Ua(T_a-T)}{\dot{m}_c C_{P,c}}=\frac{dT_a}{dV}$$

EB reacting fluid:

$$\frac{dT}{dV}=\frac{Ua(T_a-T)+r_A\Delta H_{rxn}}{\sum F_i C_{P,i}}$$

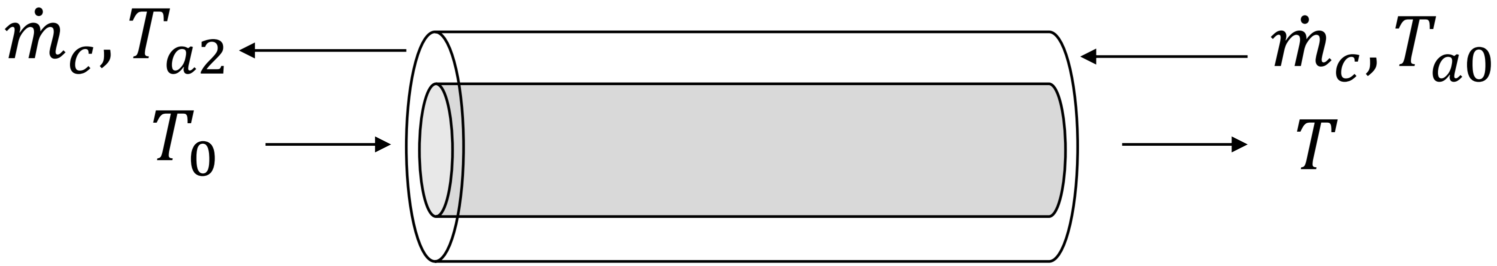
Mole balance:

$$F_{A0}\frac{dX}{dV}=-r_A$$

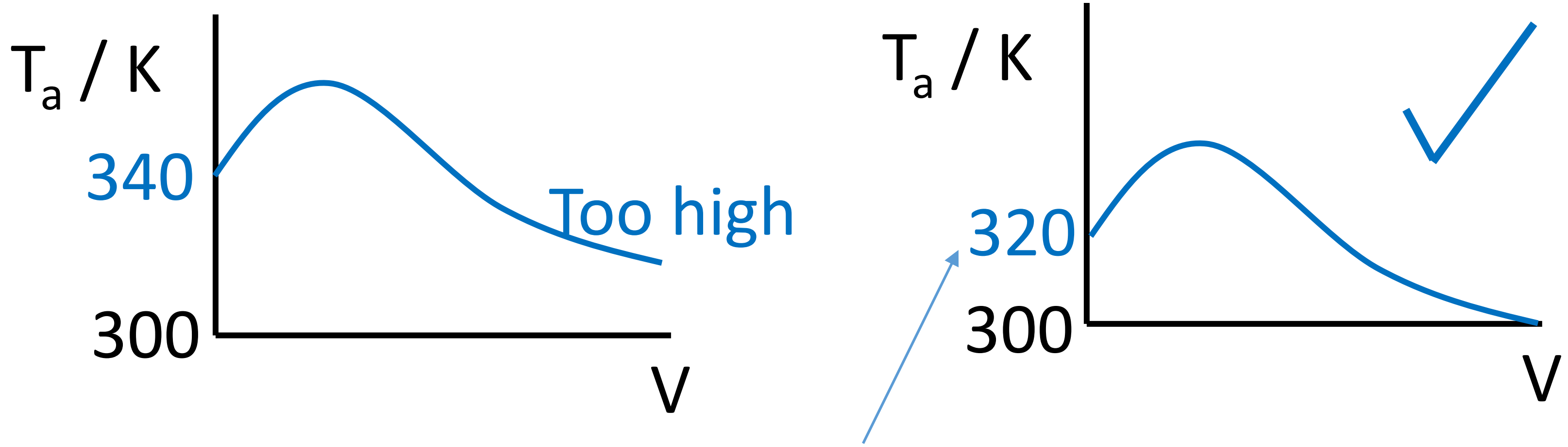
Because you do not know $T_a(V=0)=T_{a2}$ for counter current, it is harder to solve (need to do trial and error).

Example:

Countercurrent heat exchanger, exothermic reaction with T_{a0} = 300 K and known value of T_0.



Guess value of T_{a2}, solve for T_{a0}. Start with T_{a2} = 340 K



Guess a new value of T_{a2} (320 K), solve for new T_{a0} to see if it matches

Discuss with your neighbors:

For co-current PFR heat exchanger for an exothermic rxn:

If you are trying to keep a reactor from overheating using a coolant, what is true about the different temperatures?

After you have answered, think about if this would be the same for counter-current flow

A) $T_a(V=0) > T_a(V=V_{PFR})$; $T(V=0) > T(V=V_{PFR})$

[✓ B) $T_a(V=0) < T_a(V=V_{PFR})$, $T(V=V_{PFR}) > T_a(V=V_{PFR})$]

C) If $T_a(V=0) = T(V=0)$, then $T(V=V_{PFR}) < T(V=0)$

D) T is always $< T_a$

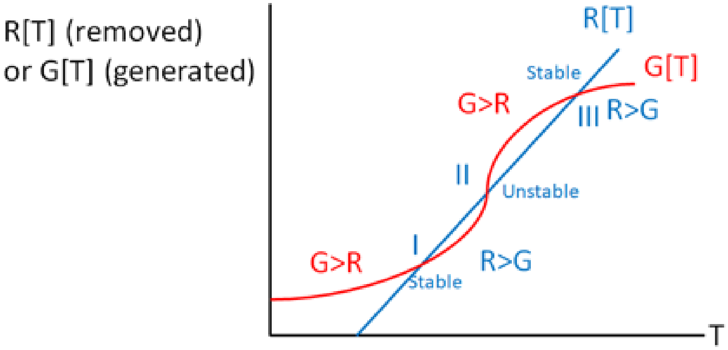
Lecture 17: Non-isothermal Reactor Design-CSTR with heat exchangers + multiple reactions
Related Text: Chapter 12.4-12.6

CSTR with high coolant flow rates:

$$\underbrace{-[\Delta H_{rxn}(T_{ref})]X}_{Reaction\ heat\ generated=G[T]} = \underbrace{C_{P0}(1+\kappa)(T-T_c)}_{\substack{Heat\ removed\ by:\\ coolant\ and\ reactor\ effluent=R[T]}}$$

$$C_{P0} \equiv \sum \theta_i C_{P,i}\,;\ \kappa \equiv \frac{UA}{F_{A0}C_{P0}};\ T_c \equiv \frac{\kappa T_a + T_0}{1+\kappa}$$

Steady states are determined when G[T] = R[T].
A steady state is stable if a perturbation from the steady state temperature would force the reactor temperature to go back to the original steady state temperature.



Multiple reactions:
Reaction 1: $A \rightarrow B;\ \Delta H_{rxn,1A} = -10\ kJ/mol\ A$
Reaction 2: $A \rightarrow 2C;\ \Delta H_{rxn,2A} = -15\ kJ/mol\ A$

For PFR: n number of reactions, involving some species j.

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + \sum_{i=1}^{n} r_{ij}\Delta H_{rxn,ij}}{\sum F_j C_{P,j}}$$

CSTR negligible shaft work, single reaction:

$$\sum -\theta_i C_{P,i}[T - T_0] - [\Delta H_{rxn}(T_{ref}) + \Delta C_P(T - T_{ref})]X + \frac{UA(T_a - T)}{F_{A0}} = 0$$

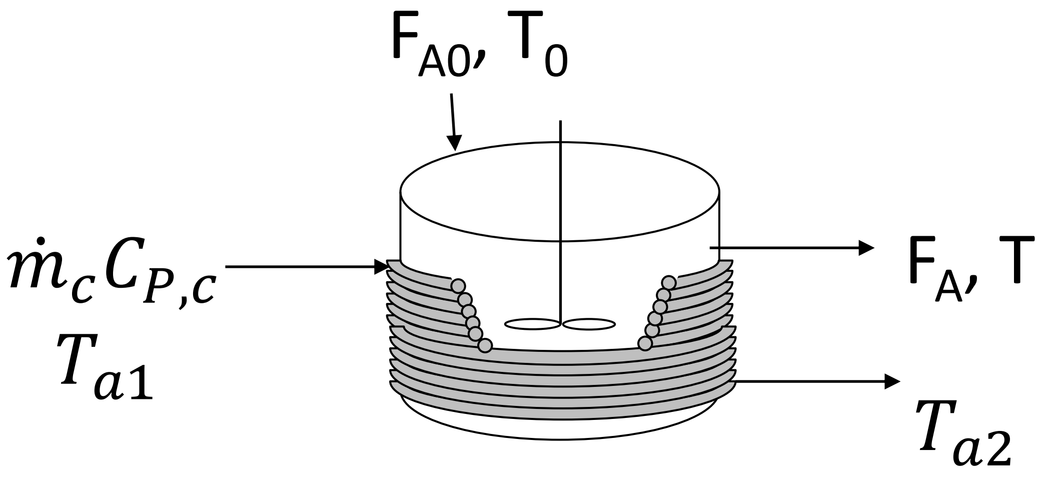
If ΔC_P=0 and re-writing without using conversion:

$$\left(\sum -\theta_i C_{P,i}[T - T_0]\right) + [\Delta H_{rxn}(T_{ref})]\frac{r_A V}{F_{A0}} + \frac{UA(T_a - T)}{F_{A0}} = 0$$

For n multiple reactions:

$$\left(\sum -\theta_j C_{P,j}[T - T_0]\right) + \frac{V}{F_{A0}}\sum_{i=1}^{n} r_{ij}\Delta H_{rxn,ij} + \frac{UA(T_a - T)}{F_{A0}} = 0$$

Non-isothermal CSTR: Possible to have multiple steady states



For CSTR, reactor itself is well mixed and uniform temperature, but feed and outlet/reactor may be at different temperatures.

$$F_{A0}\left[\left(\sum -\theta_i C_{P,i}[T - T_0]\right) - \left[\Delta H_{rxn}(T_{ref}) + \Delta C_P(T - T_{ref})\right]X\right] + \dot{Q} - \cancel{\dot{W}_{shaft}} = \cancel{\frac{d\hat{E}_{sys}}{dt}}$$

If impeller is stirring the fluid, work is done on the system so $\dot{W}_s$ would be negative (subtract a negative to get a positive).

Balance on CSTR coolant: (Derivation on Canvas)

$$\dot{m}_c C_{P,c}(\cancel{T_{a1} - T_{a2}}) - \frac{UA[\cancel{T_{a1} - T_{a2}}]}{\ln\left[\frac{T - T_{a1}}{T - T_{a2}}\right]} = 0$$

A = heat exchanger contact area , **not** shape factor (a)

$$\dot{m}_c C_{P,c} - \frac{UA}{\ln\left[\frac{T - T_{a1}}{T - T_{a2}}\right]} = 0$$

$$\ln\left[\frac{T - T_{a1}}{T - T_{a2}}\right] = \frac{UA}{\dot{m}_c C_{P,c}}$$

*Skipped step in lecture

$$\frac{T - T_{a1}}{T - T_{a2}} = \exp\left[\frac{UA}{\dot{m}_c C_{P,c}}\right]$$

$$T - T_{a1} = (T - T_{a2})\exp\left[\frac{UA}{\dot{m}_c C_{P,c}}\right]$$

Usually know T_{a1} because it is fed:

$$T_{a2} = T - (T - T_{a1})\exp\left[\frac{-UA}{\dot{m}_c C_{P,c}}\right]$$

For the coolant:

$$\dot{Q}_{coolant} = \dot{m}_c C_{P,c}(T_{a1} - T_{a2})$$

Plug in T_{a2}

$$\dot{Q}_{coolant} = \dot{m}_c C_{P,c}\left(T_{a1} - \left[T - (T - T_{a1})\exp\left[\frac{-UA}{\dot{m}_c C_{P,c}}\right]\right]\right)$$

This is the same $\dot{Q}$ as the reactor energy balance value, only here we are using balance on the coolant itself

$$\dot{Q}_{coolant} = \dot{m}_c C_{P,c}\left(T_{a1} - T + (T - T_{a1})\exp\left[\frac{-UA}{\dot{m}_c C_{P,c}}\right]\right)$$

$$= \dot{m}_c C_{P,c}(T_{a1} - T)\left(1 - \exp\left[\frac{-UA}{\dot{m}_c C_{P,c}}\right]\right)$$

For small value of x, exp[-x] = 1-x+… Taylor series can be approximated as 1-x. So if flow rate of coolant is very high:

$$\dot{Q}_{coolant} = \dot{m}_c C_{P,c}(T_{a1} - T)\left(1 - \left(1 - \frac{UA}{\dot{m}_c C_{P,c}}\right)\right)$$

$$\dot{Q}_{coolant} = \dot{m}_c C_{P,c}(T_{a1} - T)\frac{UA}{\dot{m}_c C_{P,c}} = UA(T_{a1} - T)$$

The above assumption (at high coolant flow rates) gives

$T_{a1} \approx T_{a2} \approx T_a$

$$F_{A0}\left[\left(\sum -\theta_i C_{P,i}[T-T_0]\right) - \left[\Delta H_{rxn}(T_{ref}) + \Delta C_P(T-T_{ref})\right]X\right] + \overset{UA(T_{a1}-T)}{\overset{\big\downarrow}{\dot{Q}}} - \cancel{\dot{W}_{shaft}} = \cancel{\frac{d\hat{E}_{sys}}{dt}}$$

$$\left(\sum -\theta_i C_{P,i}[T-T_0]\right) - \left[\Delta H_{rxn}(T_{ref}) + \Delta C_P(T-T_{ref})\right]X + \frac{UA(T_a - T)}{F_{A0}} = 0$$

If ΔC_P is zero:

$$\sum -\theta_i C_{P,i}[T - T_0] - \left[\Delta H_{rxn}\left(T_{ref}\right)\right]X + \frac{UA(T_a - T)}{F_{A0}} = 0$$

$$\frac{\left(\sum -\theta_i C_{P,i}[T - T_0]\right) + \frac{UA(T_a - T)}{F_{A0}}}{\Delta H_{rxn}\left(T_{ref}\right)} = X$$

Energy balance equation, coupled with mole balance:

$$\left(-\sum \theta_i C_{P,i}[T - T_0]\right) - \Delta H_{rxn}\left(T_{ref}\right)X + \frac{UA(T_a - T)}{F_{A0}} = 0$$

Mole balance for CSTR: $V = \frac{F_{A0}X}{-r_A(X,T)}$

Define a few parameters to help simplify:

$$C_{P0} \equiv \sum \theta_i C_{P,i} \qquad \kappa \equiv \frac{UA}{F_{A0} C_{P0}} \qquad T_c \equiv \frac{\kappa T_a + T_0}{1 + \kappa}$$

Rewrite energy balance:

$$-C_{P0}[T - T_0] - [\Delta H_{rxn}(T_{ref})]X + \kappa C_{P0}(T_a - T) = 0$$

$$-[\Delta H_{rxn}(T_{ref})]X = (1 + \kappa) C_{P0} T - C_{P0}(T_0 + \kappa T_a)$$

$$\underbrace{-[\Delta H_{rxn}(T_{ref})]X}_{Reaction\ heat\ generated} = (1 + \kappa) C_{P0} T - C_{P0}(T_c)(1 + \kappa)$$

$$= \underbrace{C_{P0}(1 + \kappa)(T - T_c)}_{\substack{Heat\ removed\ by: \\ coolant\ and\ reactor\ effluent}}$$

Non-isothermal, steady state CSTR algorithm

$$\underbrace{-\left[\Delta H_{rxn}\left(T_{ref}\right)\right]X}_{Reaction\ heat\ generated} = \underbrace{C_{P0}(1+\kappa)(T-T_c)}_{\substack{Heat\ removed\ by: \\ coolant\ and\ reactor\ effluent}}$$

<u>T specified</u>

$$X = \frac{C_{P0}(1+\kappa)(T-T_c)}{-\left[\Delta H_{rxn}\left(T_{ref}\right)\right]}$$

<u>X specified</u>

$$T = \frac{-\left[\Delta H_{rxn}\left(T_{ref}\right)\right]X}{C_{P0}(1+\kappa)} + T_c$$

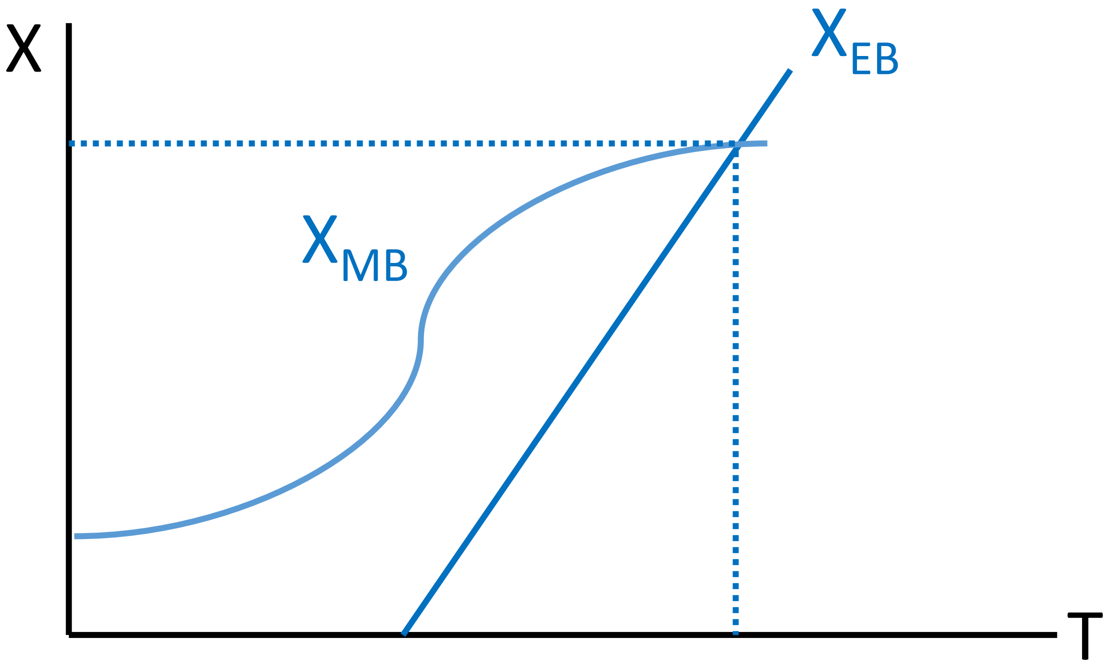
$$V = \frac{F_{A0}X}{-r_A(X, k(T))}$$

V specified

$$X_{EB} = \frac{C_{P0}(1+\kappa)(T-T_c)}{-\left[\Delta H_{rxn}\left(T_{ref}\right)\right]} \qquad V = \frac{F_{A0}X_{MB}}{-r_A(X_{MB},T)}$$

Plot both (X vs. T) and find intercepts

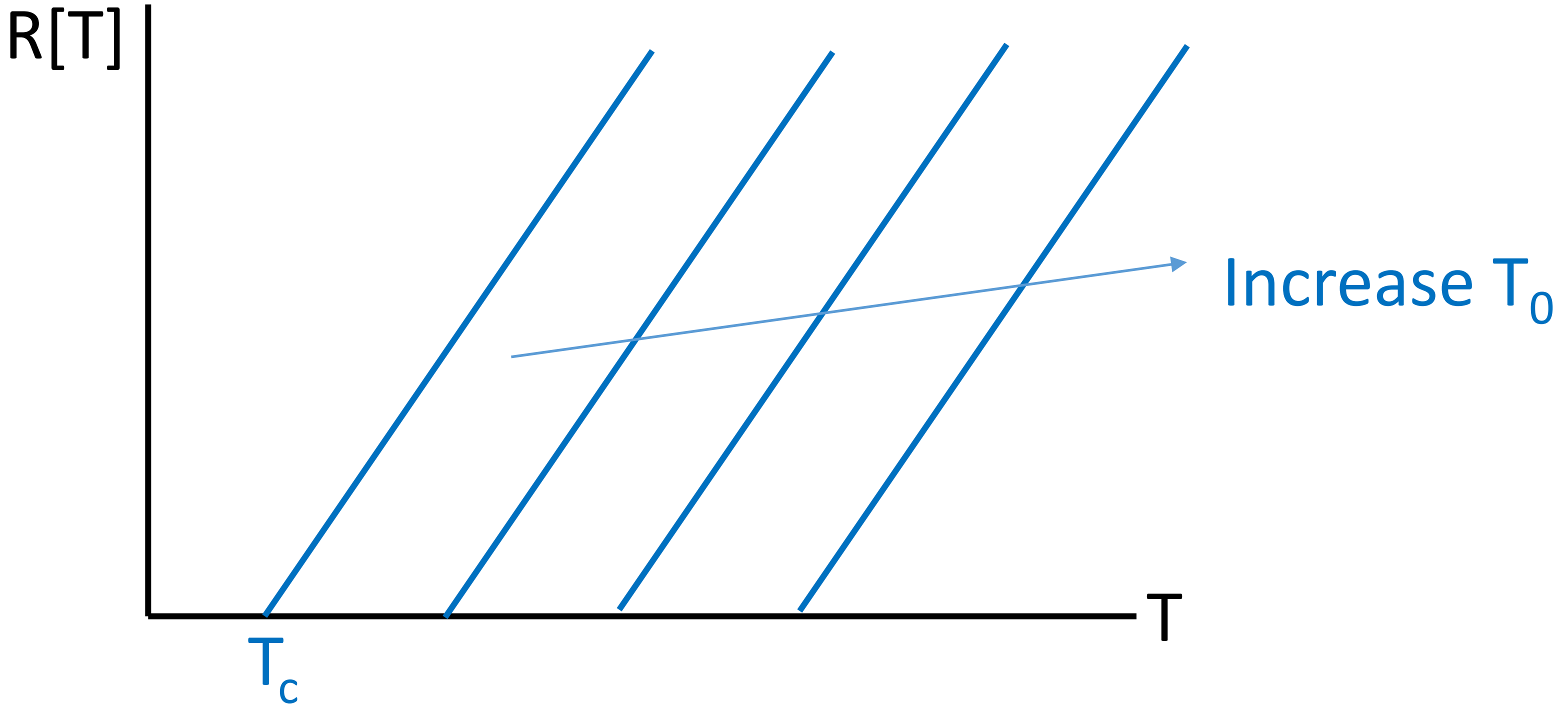
$X_{EB} = X_{MB}$



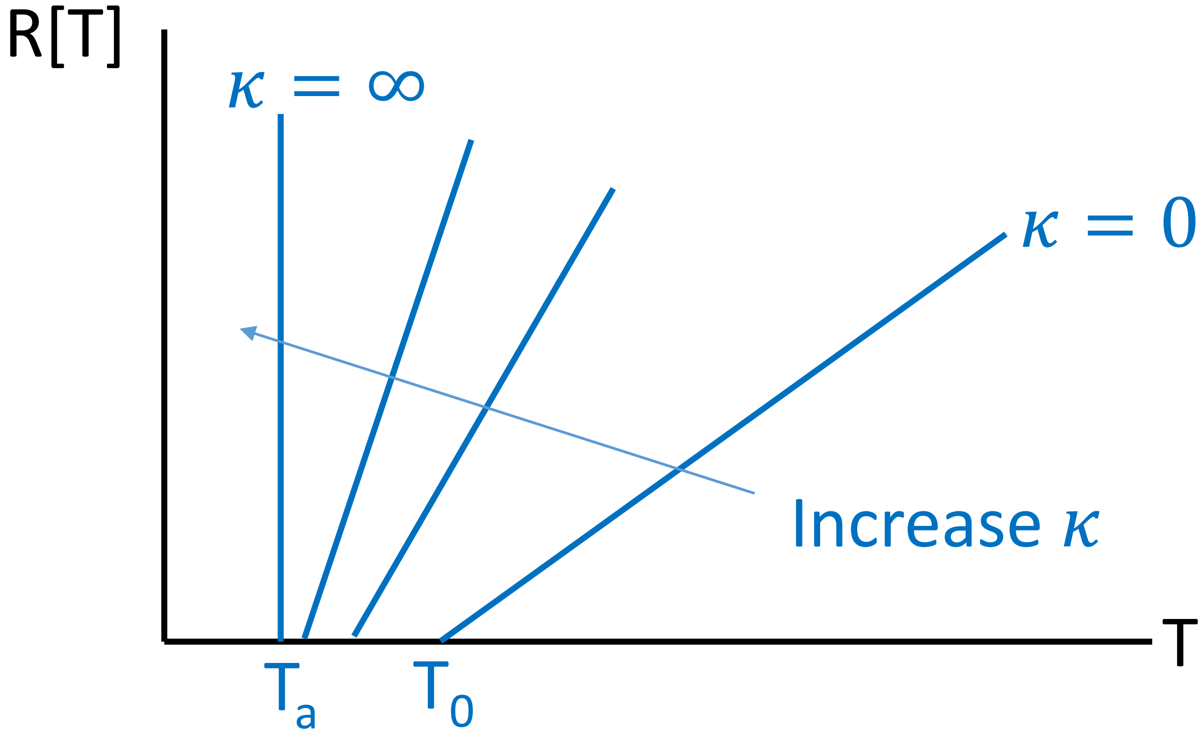
Finding steady states from generation and removal terms:

$$\underbrace{-\left[\Delta H_{rxn}\left(T_{ref}\right)\right]X}_{Reaction\ heat\ generated=G(T)} = \underbrace{C_{P0}(1+\kappa)(T-T_c)}_{\substack{Heat\ removed\ by:\\ coolant\ and\ reactor\ effluent=R(T)}}$$

$$\kappa \equiv \frac{UA}{F_{A0}C_{P0}};T_c \equiv \frac{\kappa T_a + T_0}{1+\kappa}$$



Removal term will depend on κ, T_0, T_c



$$\kappa = 0; T_c = T_0$$

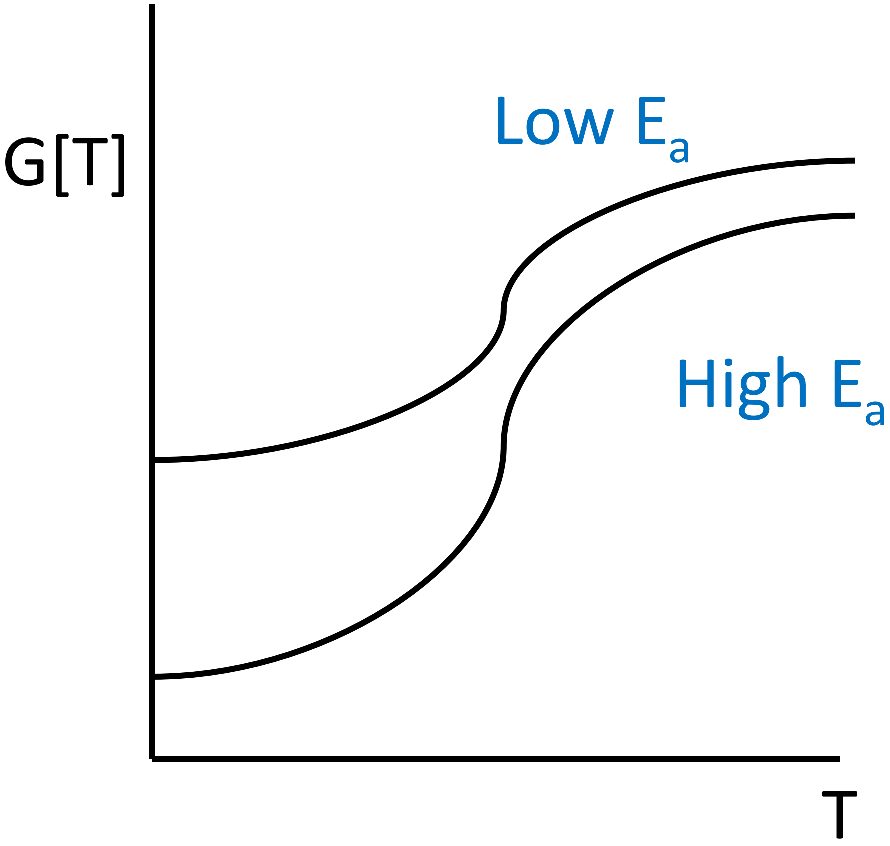
$$\kappa = \infty; T_c = T_a$$

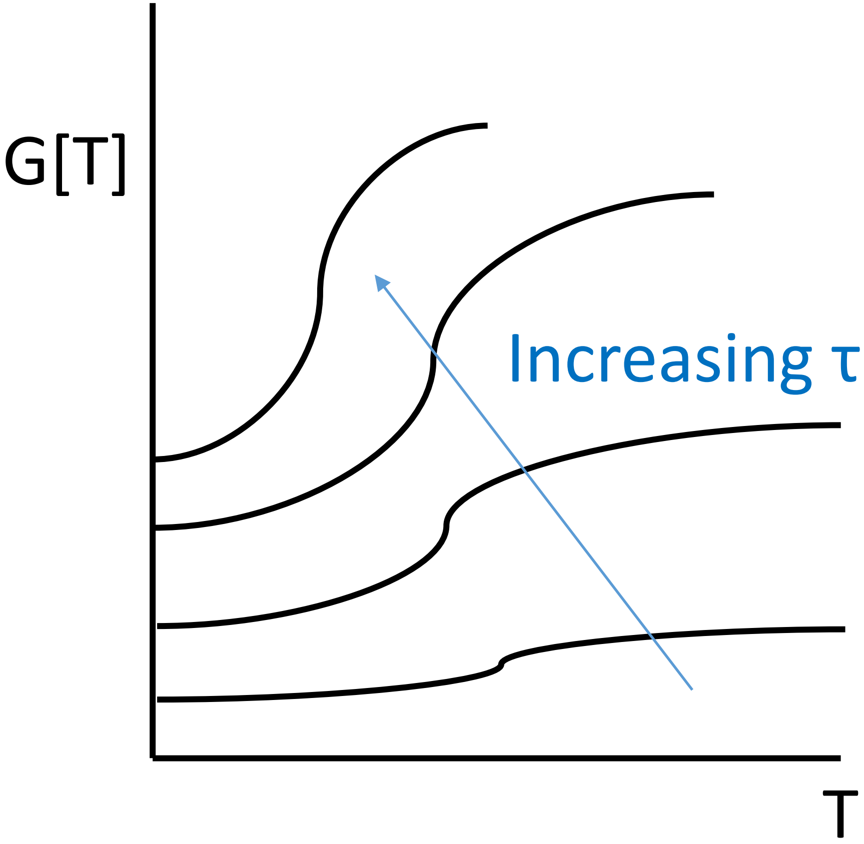
G[T] is influenced by temperature through rate coefficient k(T), and space time

$$\mathrm{G[T]} = -\left[\Delta H_{rxn}\left(T_{ref}\right)\right]X$$

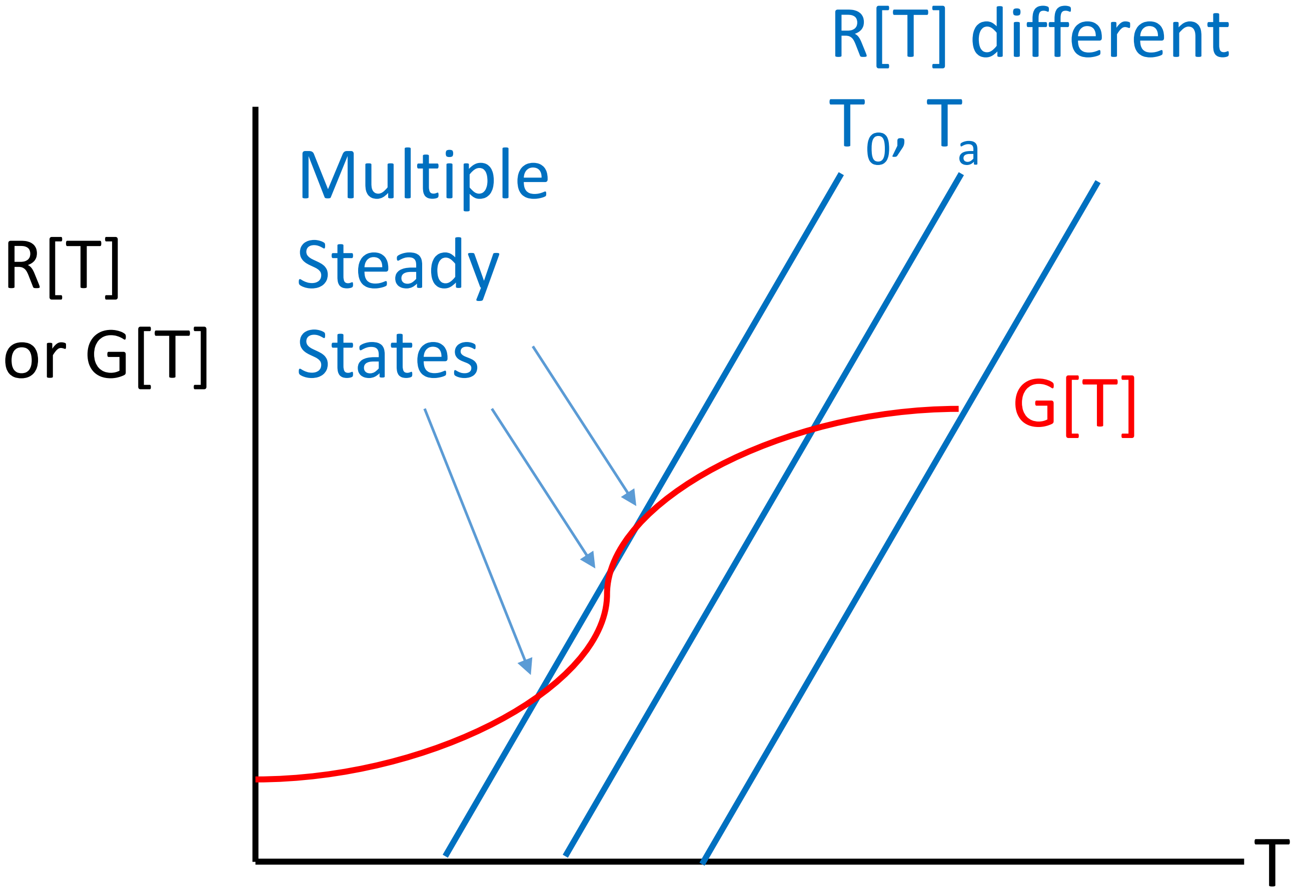
$$X = \frac{\tau k}{1+\tau k}$$

first order reaction



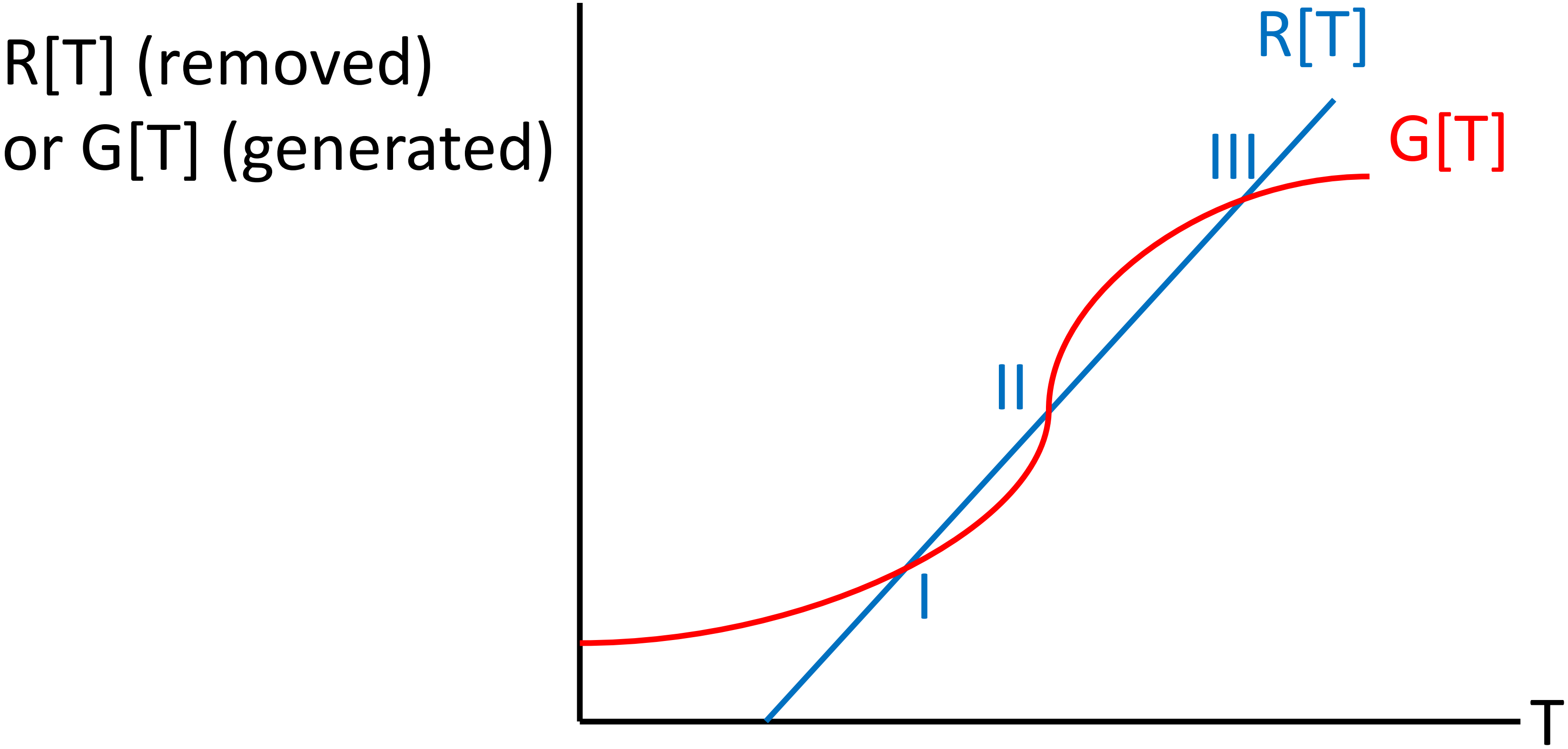


Steady state CSTR solutions are at the intersection of removal and generation terms (when generation exactly equals removal, then there will be no temperature change in time)



Stability of steady states are based on what occurs with slight perturbations to the reactor temperature.

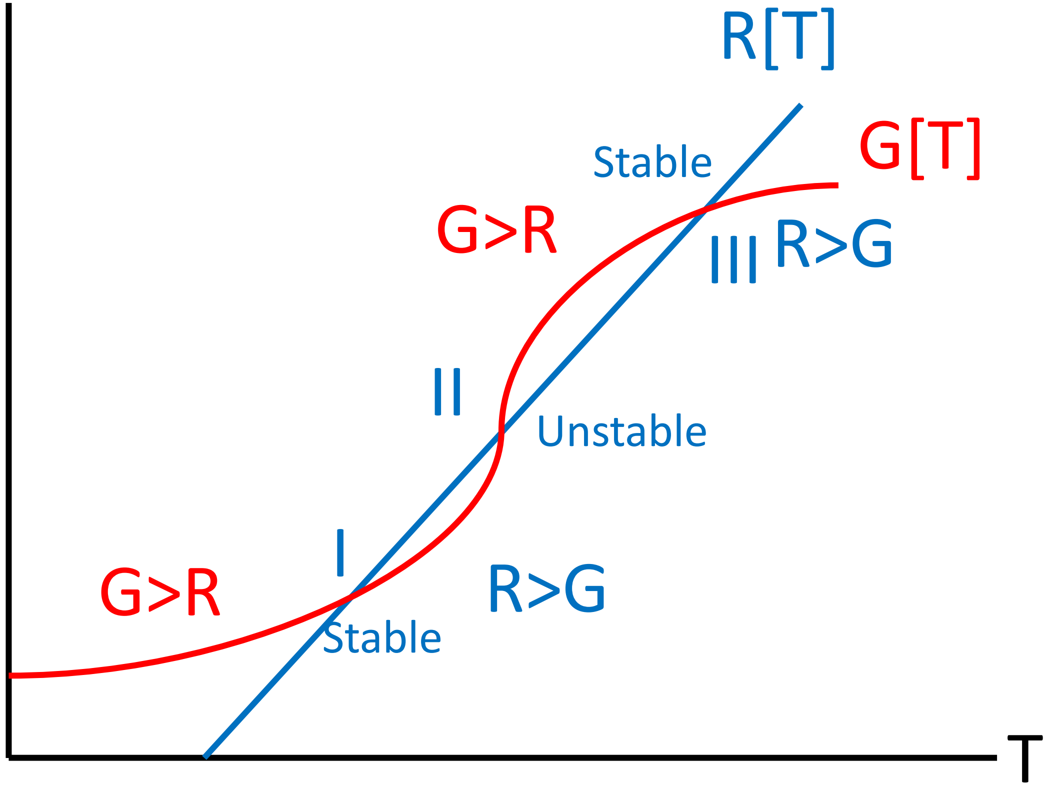
- Identify steady states (G = R), I, II, III
- G > R or R > G if you moved slightly off those T positions?
- Which way would that move the T (of reactor)?



Discuss with your neighbors:

At the steady state points we identified:

R[T] (removed)
or G[T] (generated)



A) I and III stable, II unstable

B) All unstable

C) I and III unstable, II stable

D) Only I is stable

Multiple reactions for PFR and CSTR

PFR for one reaction:

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + r_A \Delta H_{rxn}}{\sum F_i C_{P,i}}$$

PFR for multiple reactions:

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + \sum_{i=1}^{n} r_{ij} \Delta H_{rxn,ij}}{\sum F_j C_{P,j}}$$

CSTR for one reaction (with negligible shaft work)

$$\sum -\theta_i C_{P,i}[T - T_0] - \left[\Delta H_{rxn}\left(T_{ref}\right) + \Delta C_P\left(T - T_{ref}\right)\right]X$$

$$+ \frac{UA(T_a - T)}{F_{A0}} = 0$$

Assume ΔC_P=0, and recall don't want conversions:

$$\left(\sum -\theta_i C_{P,i}[T - T_0]\right) + \left[\Delta H_{rxn}(T_{ref})\right]\frac{r_A V}{F_{A0}} + \frac{UA(T_a - T)}{F_{A0}} = 0$$

CSTR multiple reactions

$$\left(\sum -\theta_j C_{P,j}[T - T_0]\right) + \frac{V}{F_{A0}}\sum_{i=1}^{n} r_{ij}\Delta H_{rxn,ij} + \frac{UA(T_a - T)}{F_{A0}} = 0$$

What does $r_{ij}\Delta H_{rxn,ij}$ mean? i refers to the number of the reaction, j refers to the limiting species that $\Delta H_{rxn,ij}$ is defined for. So if you had: $A \rightarrow B; A \rightarrow 2C$

You would have r_{1A} and r_{2A}, each with a different heat of reaction with respect to A.