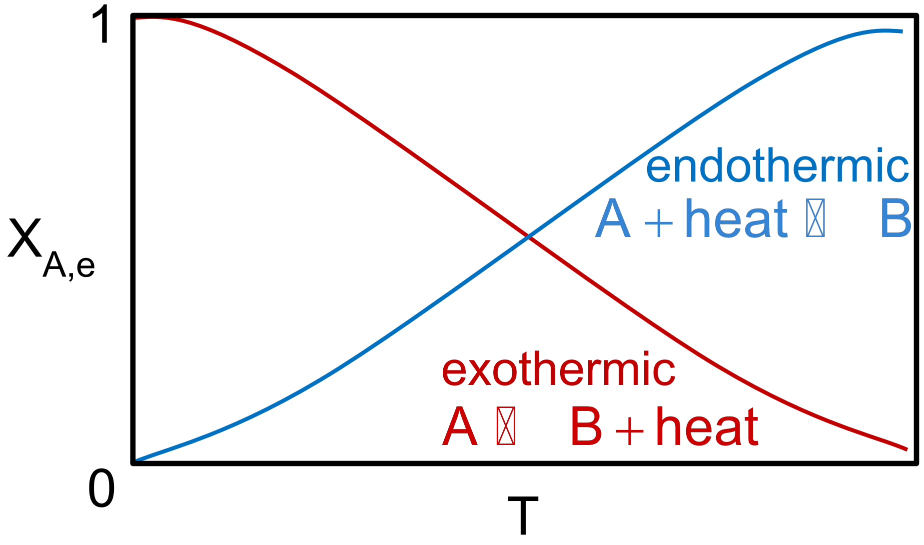
Review: Equilibrium Conversion X_{Ae}



Example) $A \rightleftharpoons B$ $C_{A0}=1$ $C_{B0}=0$

$$K_C = \frac{C_{Be}}{C_{Ae}} = \frac{\cancel{C_{A0}}\left(0 + X_{Ae}\right)}{\cancel{C_{A0}}\left(1 - X_{Ae}\right)} \rightarrow K_C = \frac{X_{Ae}}{1 - X_{Ae}}$$

Rearrange to solve in terms of X_{Ae}

$$\rightarrow K_C\left(1 - X_{Ae}\right) = X_{Ae} \quad \rightarrow K_C = X_{Ae} + K_C X_{Ae} \quad \rightarrow K_C = X_{Ae}\left(1 + K_C\right)$$

$$\rightarrow \boxed{\frac{K_C}{\left(1 + K_C\right)} = X_{Ae}}$$

This equation enables us to express X_{ae} as a function of T

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Review: X_{Ae} and Temperature

$$X_{Ae}=\frac{1}{\frac{1}{K_C(T_2)}\exp\left[\frac{\Delta H^{\circ}_{RX}(T_R)}{R}\left(\frac{1}{T}-\frac{1}{T_2}\right)\right]+1}$$

Clicker question material

Exothermic & $\Delta C_P=0$: $\Delta H^{\circ}_{RX}(T_R)<0$, when T ↑ $\exp\left[\frac{\Delta H^{\circ}_{RX}(T_R)}{R}\left(\frac{1}{T}-\frac{1}{T_2}\right)\right]\uparrow$ & $X_{Ae}\downarrow$

Makes sense from Le Chatelier's principle $A \rightleftarrows B+\text{heat}$

Exothermic rxn produces heat→
increasing temp adds heat (product) & pushes rxn to left (lower conversion)

Endothermic & $\Delta C_p\approx 0$: $\Delta H^{\circ}_{RX}(T_R)>0$, when T ↑ $\exp\left[\frac{\Delta H^{\circ}_{RX}(T_R)}{R}\left(\frac{1}{T}-\frac{1}{T_2}\right)\right]\downarrow$ & $X_{Ae}\uparrow$

Makes sense from Le Chatelier's principle $A+\text{heat} \rightleftarrows B$

Heat is a reactant in an endothermic rxn→
increasing temp adds reactant (heat) & pushes rxn to right (higher conversion)

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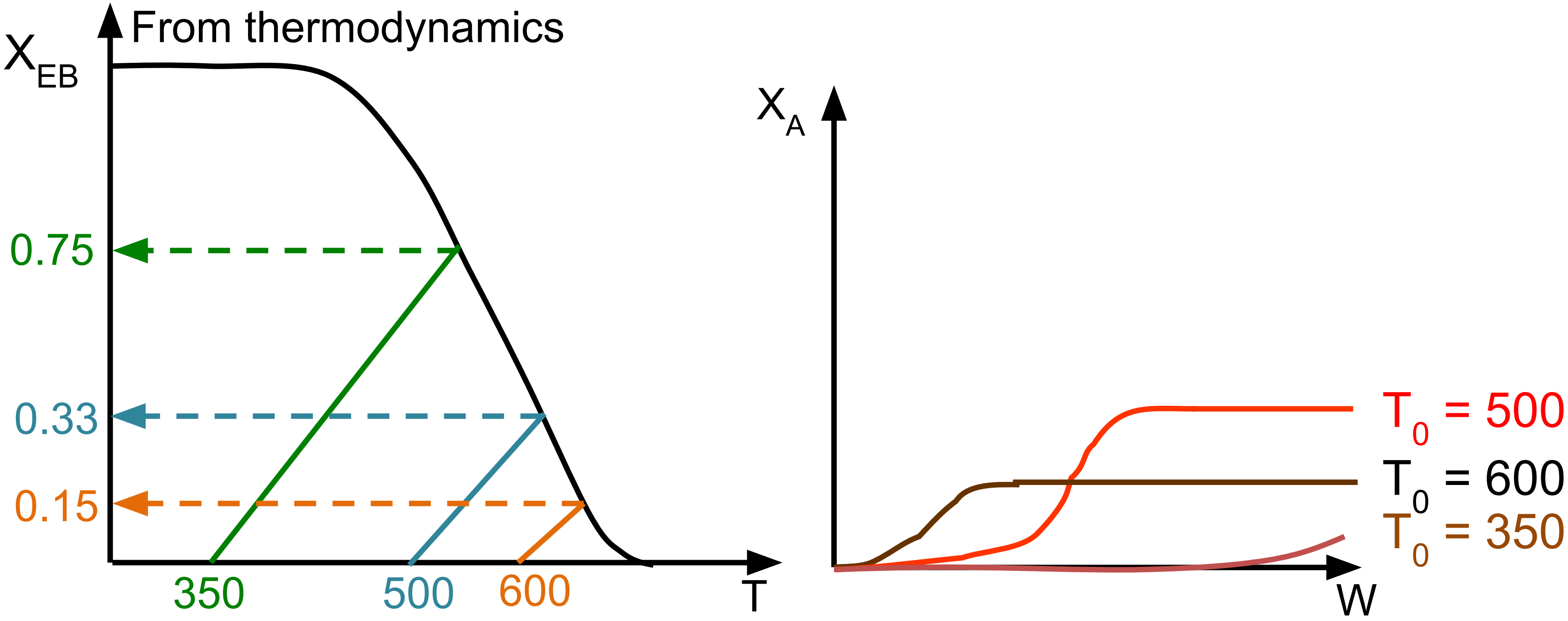
Review: Optimum Feed Temperature

For reversible, exothermic rxns, optimize feed temperature to maximize X_A

High T_0: moves $X_{A,EB}$ line to the right. Rxn reaches equilibrium fast, but low X_A

Low T_0 would give high $X_{A,e}$ but the specific reaction rate k is so small that most of the reactant passes through the reactor without reacting (never reach $X_{A,e}$)



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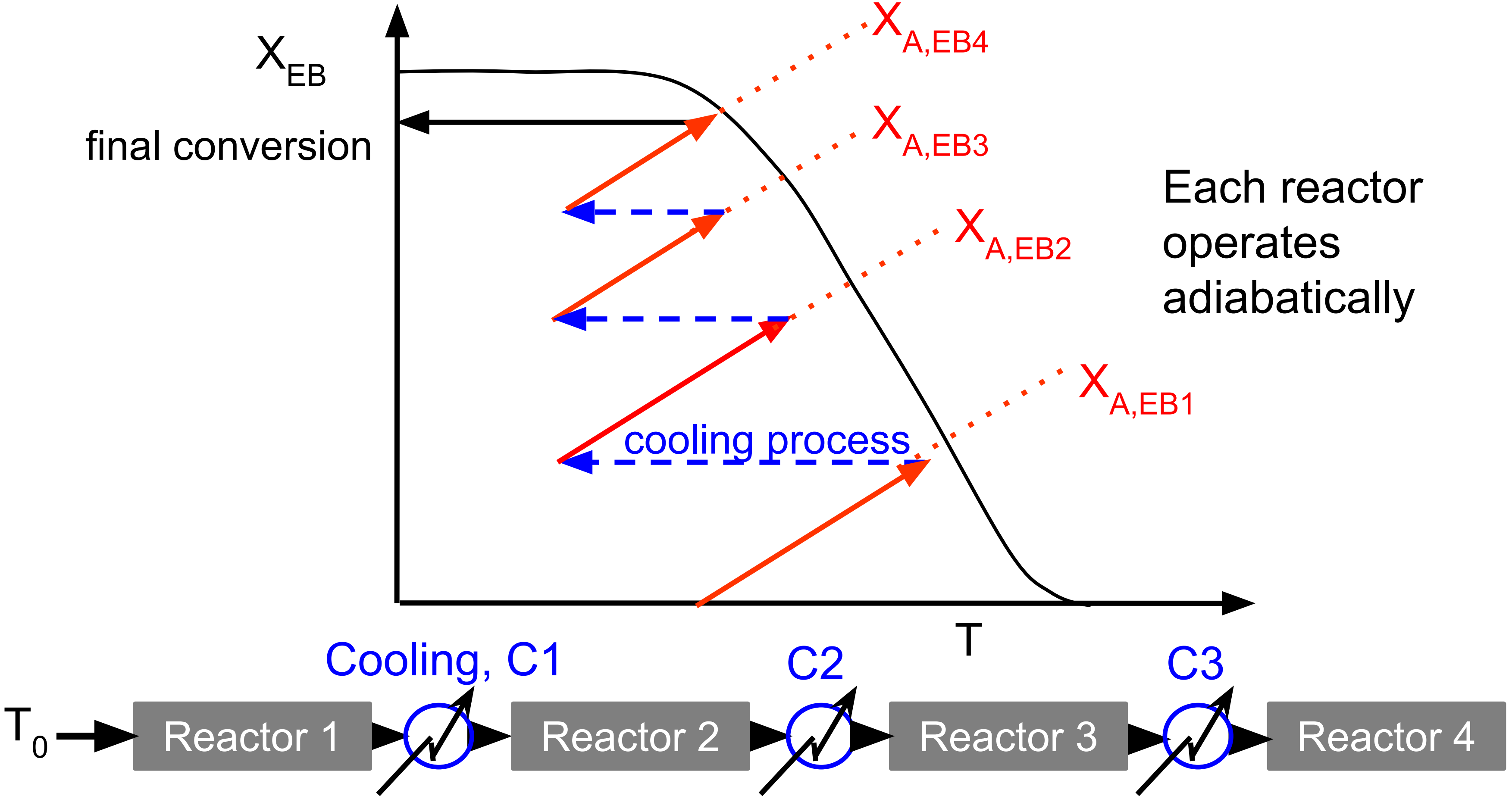
Review: Interstage Cooling

- Adiabatic operation of each reactor simplifies the energy balance
- Higher feed temp- reaction reaches equilibrium quickly but $X_{A,e}$ is low
- Lower feed temp- higher $X_{A,e}$ but reaction rate is too slow to be practical
- Cooling between reactors shifts $X_{A,EB}$ line to the left, increasing X_A



Each reactor operates adiabatically

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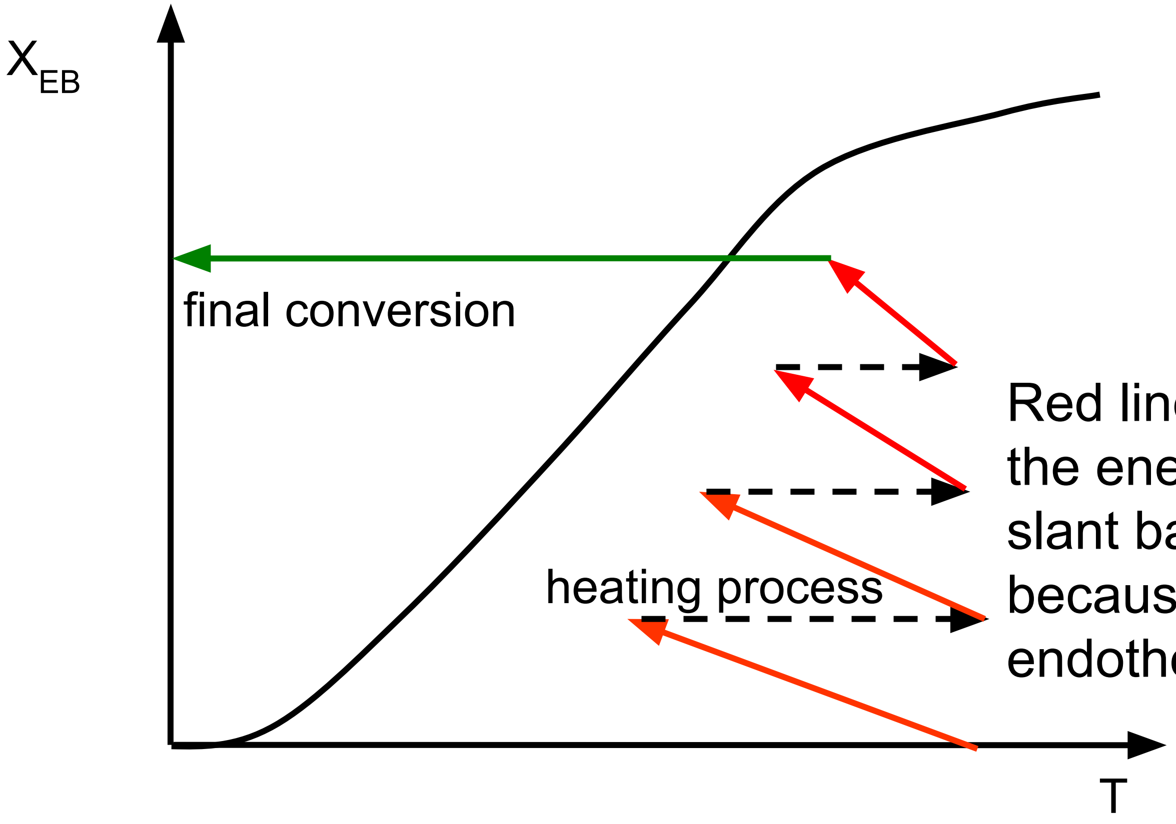
Review: Endothermic Reactions

The equilibrium conversion increases with increasing temperature, so use <u>interstage heating</u> to increase the conversion



Red lines are from the energy balance, slant backwards because $\Delta H^\circ_{RX} > 0$ for endothermic reaction

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L14: Nonadiabatic PFR/PBR Operation and Reactor Stability

1. T changes with distance down reactor- differential form of EB must be used
2. Multiple steady states: more than one set of conditions satisfies both the energy balance & mole balance

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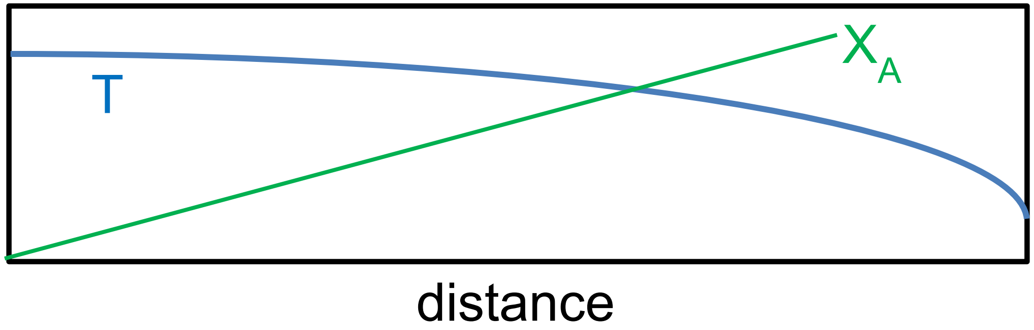
Review: Application to a SS PFR



Negligible shaft work ($\dot{W}_S$=0) and adiabatic ($\dot{Q}$=0)

- a) Use TEB to construct a table of T as a function of X_A
- b) Use $k = Ae^{-E/RT}$ to obtain k as a function of X_A
- c) Use stoichiometry to obtain $-r_A$ as a function of X_A
- d) Calculate:

$$V = F_{A0} \int_{X_{A0}}^{X_A} \frac{dX_A}{-r_A(X_A, T)}$$

may use numerical methods

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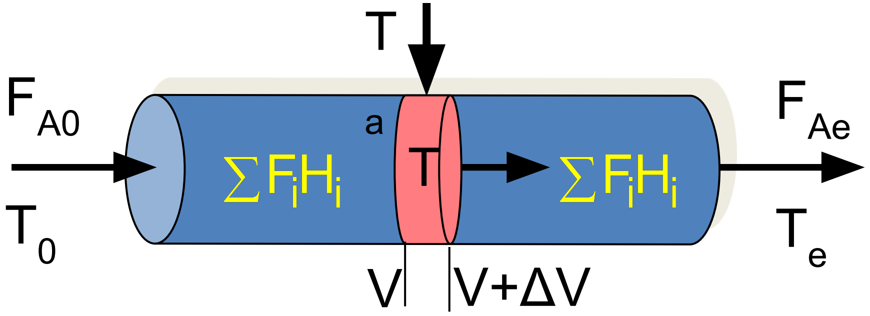
Steady-State PFR/PBR w/ Heat Exchanger

Heat is added or removed through the cylindrical walls of the reactor

$$\dot{Q} = U\Delta A\left(T_a - T\right) = Ua\left(T_a - T\right)\Delta V$$

$$a = \frac{A}{V}$$



Heat exchange area per volume of reactor

Energy balance on small volume of SS PFR:

$$\Delta\dot{Q} - \underset{0}{\cancel{\dot{W}_s}} + \sum F_i H_i\Big|_V - \sum F_i H_i\Big|_{V+\Delta V} = 0$$

Plug in Q: $\rightarrow Ua\left(T_a - T\right)\Delta V - \dot{W}_s + \sum F_i H_i\Big|_V - \sum F_i H_i\Big|_{V+\Delta V} = 0$

Take limit as ΔV→∞: $\rightarrow Ua\left(T_a - T\right) - \dfrac{d\sum\left(F_i H_i\right)}{dV} = 0$

Expand: $\rightarrow Ua\left(T_a - T\right) - \dfrac{\sum dF_i}{dV} H_i - \sum F_i \dfrac{dH_i}{dV} = 0$

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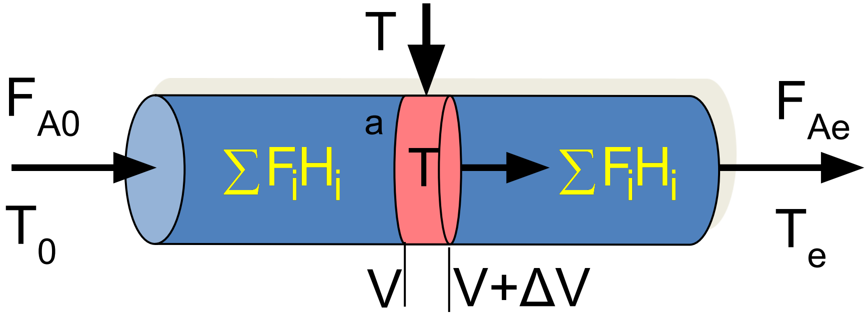
TEB for PFR/PBR w/ Heat Exchanger



$$Ua(T_a - T) - \frac{\sum dF_i}{dV} H_i - \sum F_i \frac{dH_i}{dV} = 0$$

Substitute the differentials: $\frac{dF_i}{dV} = r_i = \nu_i(-r_A)$ and $\frac{dH_i}{dV} = C_{pi}\frac{dT}{dV}$

$$\rightarrow Ua(T_a - T) - \sum H_i \nu_i(-r_A) - \sum F_i C_{Pi}\frac{dT}{dV} = 0 \qquad \sum \nu_i H_i = \Delta H_{RX}$$

$$\rightarrow Ua(T_a - T) - \Delta H_{RX}(-r_A) - \sum F_i C_{Pi}\frac{dT}{dV} = 0$$

Solve for dT/dV:

$$\rightarrow -\sum F_i C_{Pi}\frac{dT}{dV} = \Delta H_{RX}(-r_A) - Ua(T_a - T) \quad \rightarrow \frac{dT}{dV} = \frac{\Delta H_{RX}(r_A) + Ua(T_a - T)}{\sum F_i C_{Pi}}$$

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Energy Balance for Tubular Reactors

$$\frac{dT}{dV}=\frac{\overbrace{\Delta H_{RX}(r_A)}^{\text{Heat generated}}+\overbrace{Ua(T_a-T)}^{\text{Heat removed}}}{\sum F_iC_{Pi}}$$

Multiply Ua and (T_a-T) by -1 (-1 x -1 = 1)→

$$\frac{dT}{dV}=\frac{\overbrace{\Delta H_{RX}(r_A)}^{\text{Heat generated}}-\overbrace{Ua(T-T_a)}^{\text{Heat removed}}}{\sum F_iC_{Pi}}$$

Switched sign & order in bracket

$$\left.\begin{aligned}\Delta H_{RX}&=\Delta H^{\circ}_{RX}(T_R)+\Delta C_P(T-T_R)\\ F_i&=F_{A0}(\Theta_i+\nu_iX_A)\end{aligned}\right\}$$

Substitute and multiply out the denominator

$$\downarrow$$

$$\frac{dT}{dV}=\frac{\left[\Delta H^{\circ}_{RX}(T_R)+\Delta C_P(T-T_R)\right](r_A)+Ua(T_a-T)}{F_{A0}\sum\left(\Theta_iC_{Pi}+\boxed{C_{Pi}\nu_i}X_A\right)}$$

for $A\rightarrow B$

$$\nu_iC_{Pi}=\frac{b}{a}C_{PB}-C_{PA}=\Delta C_P$$

$$\rightarrow\frac{dT}{dV}=\frac{\left[\Delta H^{\circ}_{RX}(T_R)+\Delta C_P(T-T_R)\right](r_A)+Ua(T_a-T)}{F_{A0}\left(\sum\Theta_iC_{Pi}+\Delta C_PX_A\right)}$$

Energy balance for SS PFR, $\dot{W}_s$=0

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

PFR energy balance is coupled to the PFR design eq, and PFR design eq is coupled to Arrhenius eq for k or K_{equil}

(these are the 3 equations that must be simultaneously solved)

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Liquid Phase Reaction in PFR

$A \rightleftarrows B$ liquid phase rxn carried out in PFR; $\dot{W}_S = 0$ & pure A enters the PFR

✔ Mole balance
$$\frac{dX_A}{dV} = \frac{-r_A}{F_{A0}}$$

✔ Rate law
$$-r_A = k\left(C_A - \frac{C_B}{K_C}\right) \quad \text{with}$$

$$\boxed{k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]} \quad \boxed{K_C(T) = K_C(T_2)\exp\left[\frac{\Delta H^\circ_{RX}(T_R)}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right]}$$

✔ Stoichiometry
$$C_A = C_{A0}(1 - X_A) \qquad C_B = C_{A0}X_A$$

✔ Combine
$$\boxed{\frac{dX_A}{dV} = \frac{k\left[1 - X_A - X_A / K_C\right]}{\upsilon_0}}$$

✔ Energy balance
$$\boxed{\frac{dT}{dV} = \frac{\left[\Delta H^\circ_{RX}(T_R) + \Delta C_P(T - T_R)\right](r_A) + Ua(T_a - T)}{F_{A0}\left(\sum \Theta_i C_{Pi} + \Delta C_P X_A\right)}}$$

Solve these equations simultaneously with an ODE solver (Polymath)

If this were a gas phase rxn w/ pressure drop, change stoichiometry accordingly & include an equation for dΔP/dW

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Review: Nonisothermal CSTR

Isothermal CSTR: feed temp = temperature inside the CSTR

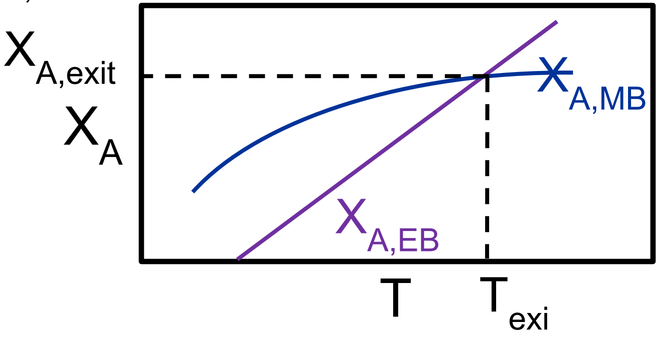
Case 1: Given F_{A0}, C_{A0}, A, E, C_{pi}, $H°_I$, and X_A, calculate T & V

a) Solve TEB for T at the exit ($T_{exit} = T_{inside\ reactor}$)
b) Calculate $k = Ae^{-E/RT}$ where T was calculated in step a
c) Plug the k calculated in step b into the design equation to calculate V_{CSTR}

Case 2: Given F_{A0}, C_{A0}, A, E, C_{pi}, $H°_I$, and V, calculate T & X_A

a) Solve TEB for T as a function of X_A
b) Solve CSTR design equation for X_A as a function of T (plug in $k = Ae^{-E/RT}$)
c) Plot $X_{A,EB}$ vs T & $X_{A,MB}$ vs T on the same graph. The intersection of these 2 lines is the conditions (T and X_A) that satisfies the energy & mass balance

$X_{A,EB}$ = conversion determined from the TEB equation
$X_{A,MB}$ = conversion determined using the design equation



Intersection is T and X_A that satisfies both equations

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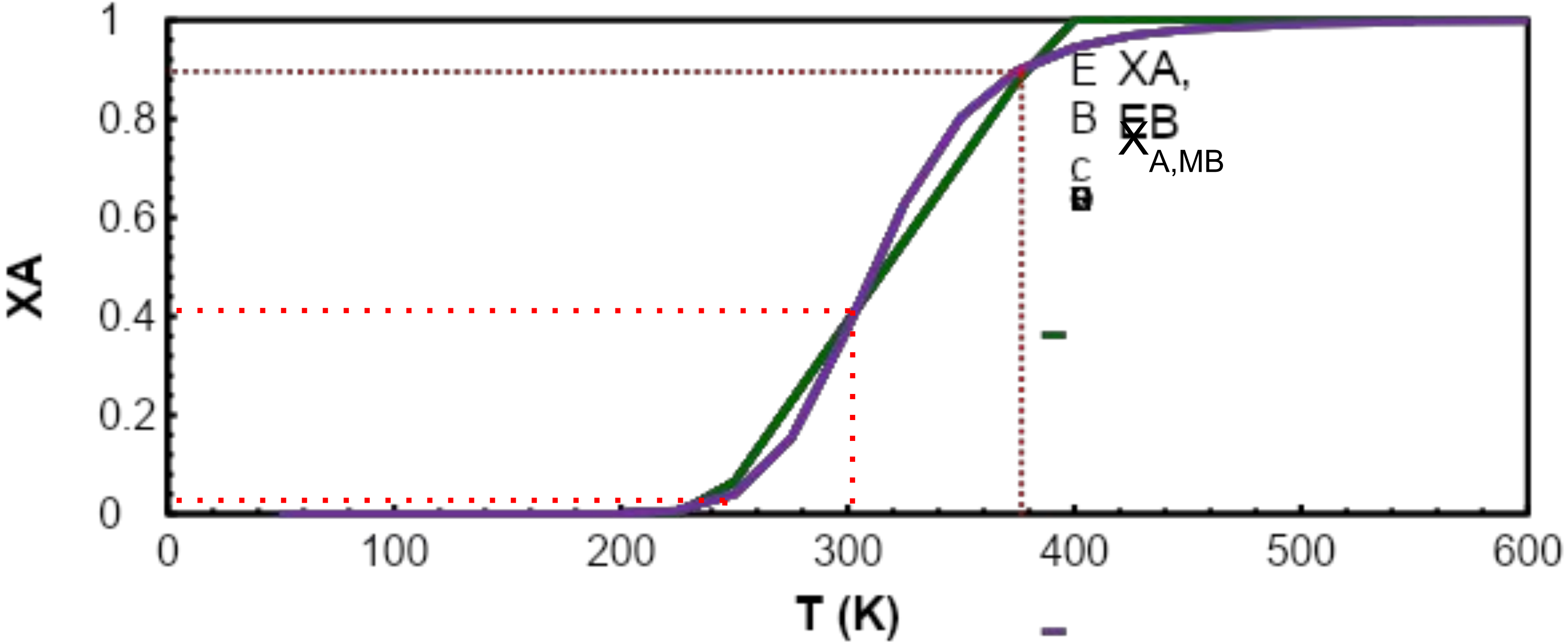
Multiple Steady States in CSTR



- Plot of $X_{A,EB}$ vs T and $X_{A,MB}$ vs T
- Intersections are the T and X_A that satisfy both the mass balance and energy balance
- Multiple sets of conditions are possible for the same rxn in the same reactor with the same inlet conditions!

Reactor must operate near one of these steady states-
this requires knowledge of their stability!

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Consider a jacketed CSTR with constant heat capacity, negligible shaft work, $\Delta C_P=0$, first order kinetics, all feeds at the same temperature ($T_{i0}=T_0$), constant T_a in jacket, and an overall heat transfer coefficient

$$\dot{Q} = UA\left(T_a - T\right)$$

$$\text{TEB}: 0 = \dot{Q} - F_{A0}\sum_{i=1}^{n}\Theta_i C_{p,i}\left[T - T_{i0}\right] - \Delta H_{RX}(T)F_{A0}X_A$$

Substituting for $\dot{Q} = UA\left(T_a - T\right)$ and $\Delta H_{RX}(T) = \Delta H_{RX}^{\circ}(T_R)$ since $\Delta C_P = 0$

$$\rightarrow 0 = UA\left(T_a - T\right) - F_{A0}\sum_{i=1}^{n}\Theta_i C_{p,i}\left[T - T_{i0}\right] - \Delta H_{RX}^{\circ}(T_R)F_{A0}X_A$$

Bring terms that remove heat to other side of equation:

$$\rightarrow F_{A0}\sum_{i=1}^{n}\Theta_i C_{p,i}\left[T - T_{i0}\right] - UA\left(T_a - T\right) = -\Delta H_{RX}^{\circ}(T_R)F_{A0}X_A$$

$$\rightarrow \underbrace{\sum_{i=1}^{n}\Theta_i C_{p,i}\left[T - T_{i0}\right] - \frac{UA\left(T_a - T\right)}{F_{A0}}}_{\text{Heat removed term} \equiv R(T)} = \underbrace{-\Delta H_{RX}^{\circ}(T_R)X_A}_{\text{Heat generated term} \equiv G(T)}$$

A steady-state occurs when $R(T) = G(T)$

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Even More Terms…

$$\overbrace{\sum_{i=1}^{n}\Theta_i C_{p,i}\left[T-T_{i0}\right]-\frac{UA\left(T_a-T\right)}{F_{A0}}}^{\text{Heat removed term} \equiv R(T)}=\overbrace{-\Delta H_{RX}^{\circ}\left(T_R\right)X_A}^{\text{Heat generated term} \equiv G(T)}$$

$$C_{P0}=\sum\Theta_i C_{Pi} \qquad V=\frac{F_{A0}X_A}{-r_A}\rightarrow\frac{-r_A V}{F_{A0}}=X_A$$

Substitute $\rightarrow C_{p0}\left[T-T_{i0}\right]-\dfrac{UA\left(T_a-T\right)}{F_{A0}}=-\Delta H_{RX}^{\circ}\left(T_R\right)\left(\dfrac{-r_A V}{F_{A0}}\right)$

More substitutions: $\kappa=\dfrac{UA}{C_{p0}F_{A0}} \quad T_c=\dfrac{T_0F_{A0}C_{p0}+UAT_a}{UA+C_{p0}F_{A0}}=\dfrac{\kappa T_a+T_0}{1+\kappa}$

$$\Delta H_{RX}^{\circ}=\Delta H_{RX}^{\circ}\left(T_R\right)$$

$$\rightarrow C_{p0}\left(1+\kappa\right)\left[T-T_C\right]=-\Delta H_{RX}^{\circ}\left(\frac{-r_A V}{F_{A0}}\right)$$

Heat removed: $R\left(T\right)=C_{p0}\left(1+\kappa\right)\left[T-T_C\right]$

Heat generated: $G\left(T\right)=-\Delta H_{RX}^{\circ}\left(\dfrac{-r_A V}{F_{A0}}\right)$

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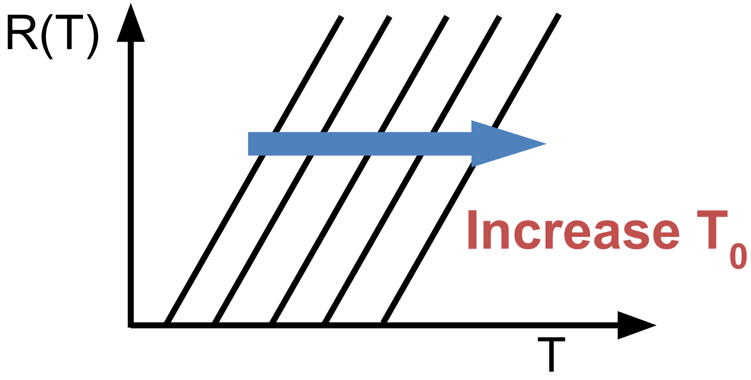
Heat Removal Term and T_0

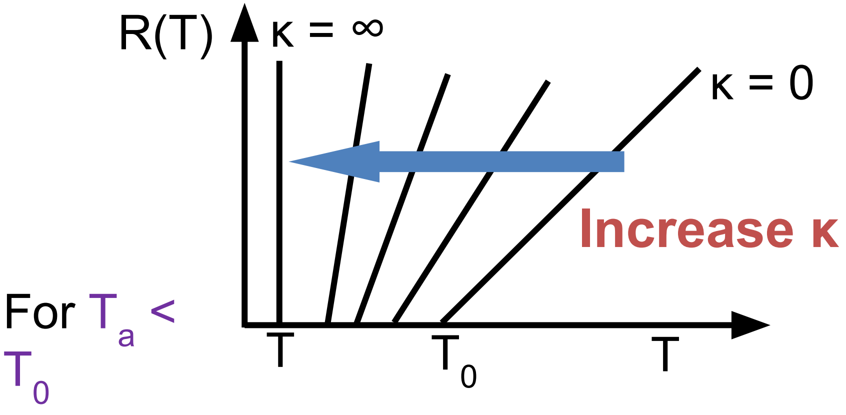
$$\overbrace{C_{p0}(1+\kappa)[T-T_C]}^{\text{Heat removed: R(T)}} = \overbrace{-\Delta H_{RX}^{\circ}\left(\frac{-r_A V}{F_{A0}}\right)}^{\text{Heat generated G(T)}}$$

$$\kappa = UA / C_{p0} F_{A0} \qquad T_C = \frac{\kappa T_a + T_0}{1+\kappa}$$

R(T) line has slope of $C_{P0}(1+\kappa)$



When T_0 increases, slope stays same & line shifts to right



When κ increases from lowering F_{A0} or increasing heat exchange, slope and x-intercept moves

$T_a < T_0$: x-intercept shifts left as κ↑

$T_a > T_0$: x-intercept shifts right as κ↑

$\kappa = 0$, then $T_C = T_0$ $\kappa = \infty$, then $T_C = T_a$

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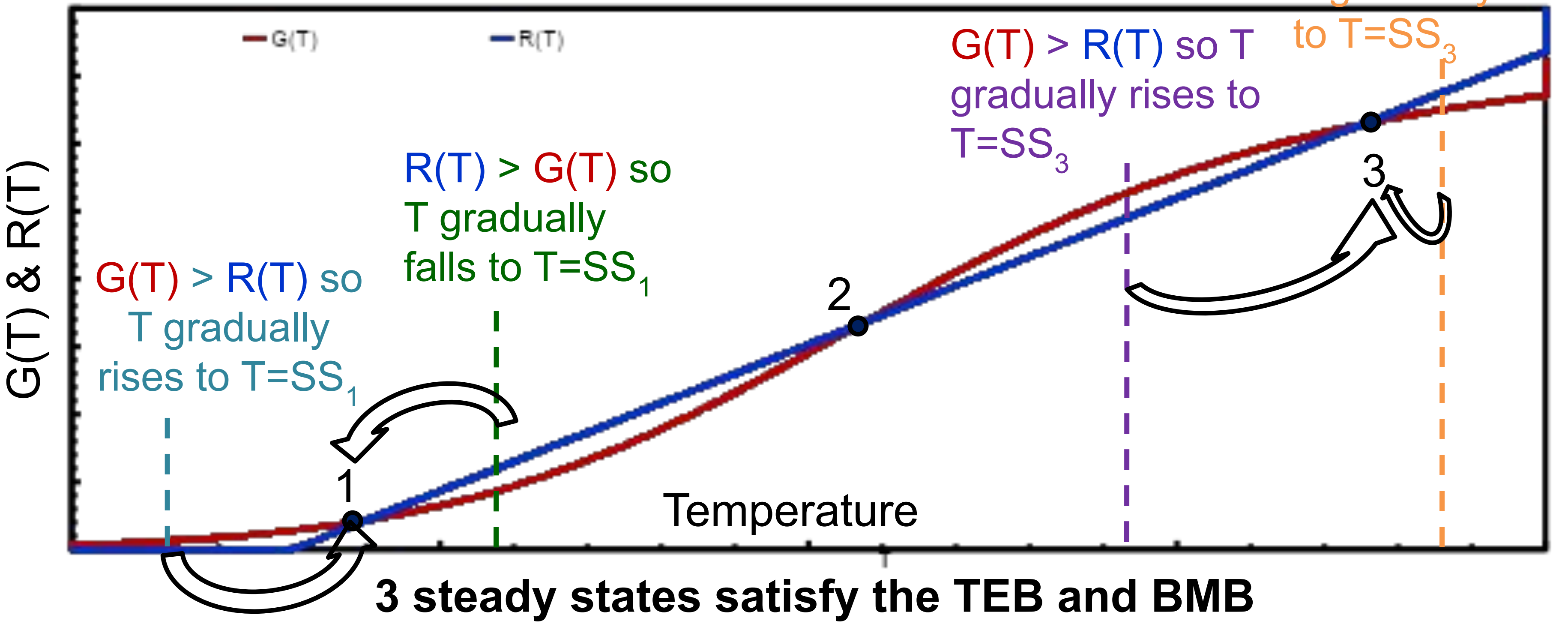
CSTR Stability



G(T) > R(T) so T gradually rises to $T=SS_1$

R(T) > G(T) so T gradually falls to $T=SS_1$

G(T) > R(T) so T gradually rises to $T=SS_3$

R(T) > G(T) so T gradually falls to $T=SS_3$

3 steady states satisfy the TEB and BMB

- Suppose a disturbance causes the reactor T to drift to a T between SS_1 & SS_2
- Suppose a disturbance causes the reactor T to drift to a T between SS_2 & SS_3
- Suppose a disturbance causes the reactor T to drop below SS_1
- Suppose a disturbance causes the reactor T to rise above SS_3

SS_1 and SS_3 are locally stable (return to them after temp pulse)

SS_2 is an unstable- do not return to SS_2 if there is a temp pulse

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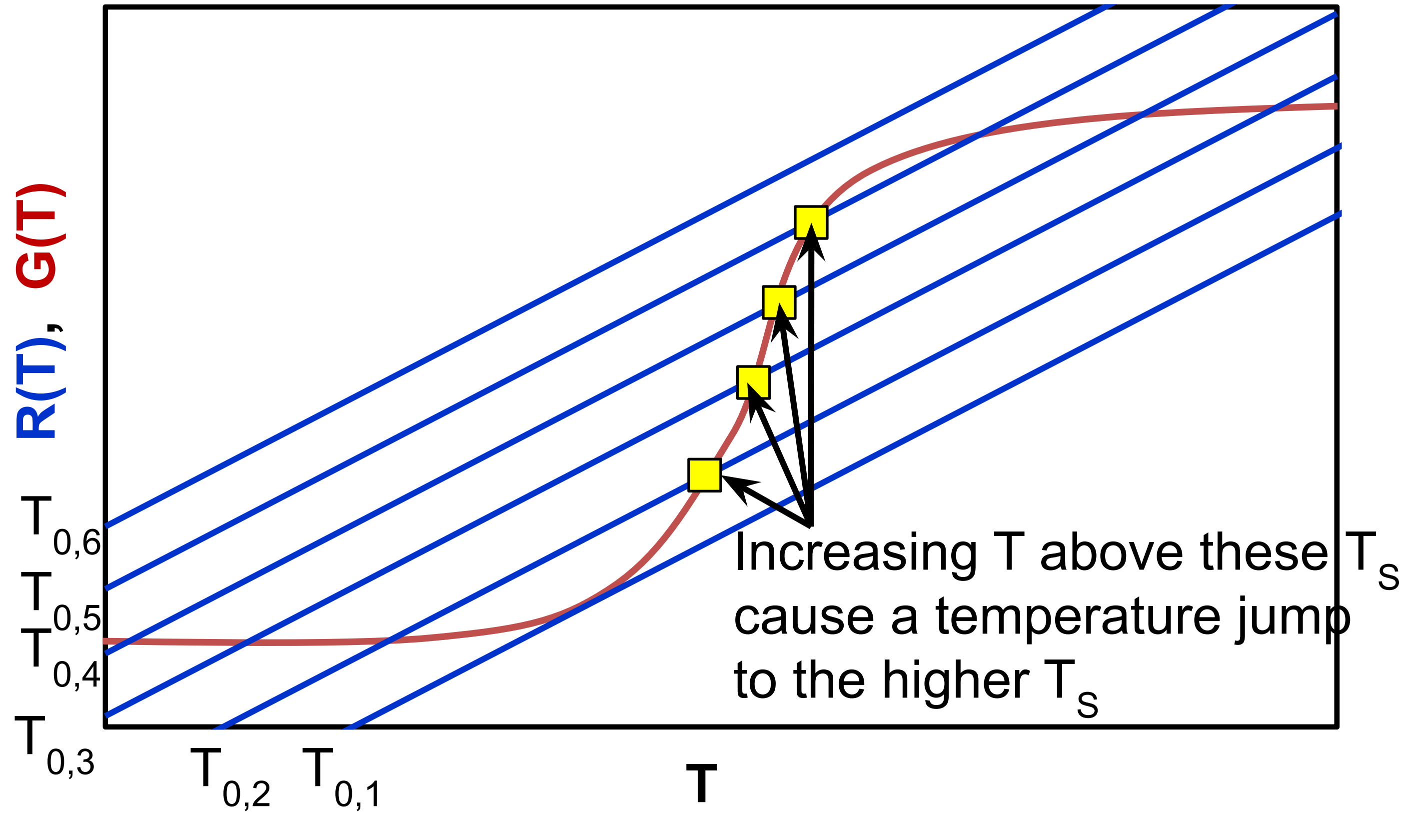
Multiple Steady States and T_0



Increasing T above these T_S cause a temperature jump to the higher T_S

- Changing the inlet T will shift the steady state temperature (T_S)
- Notice that the number of steady state temperatures depends on T_0

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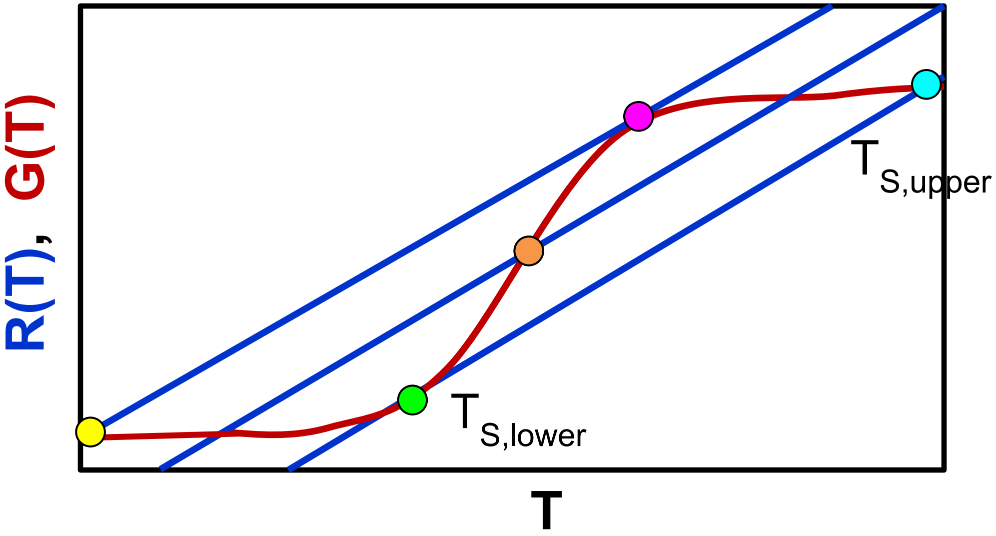
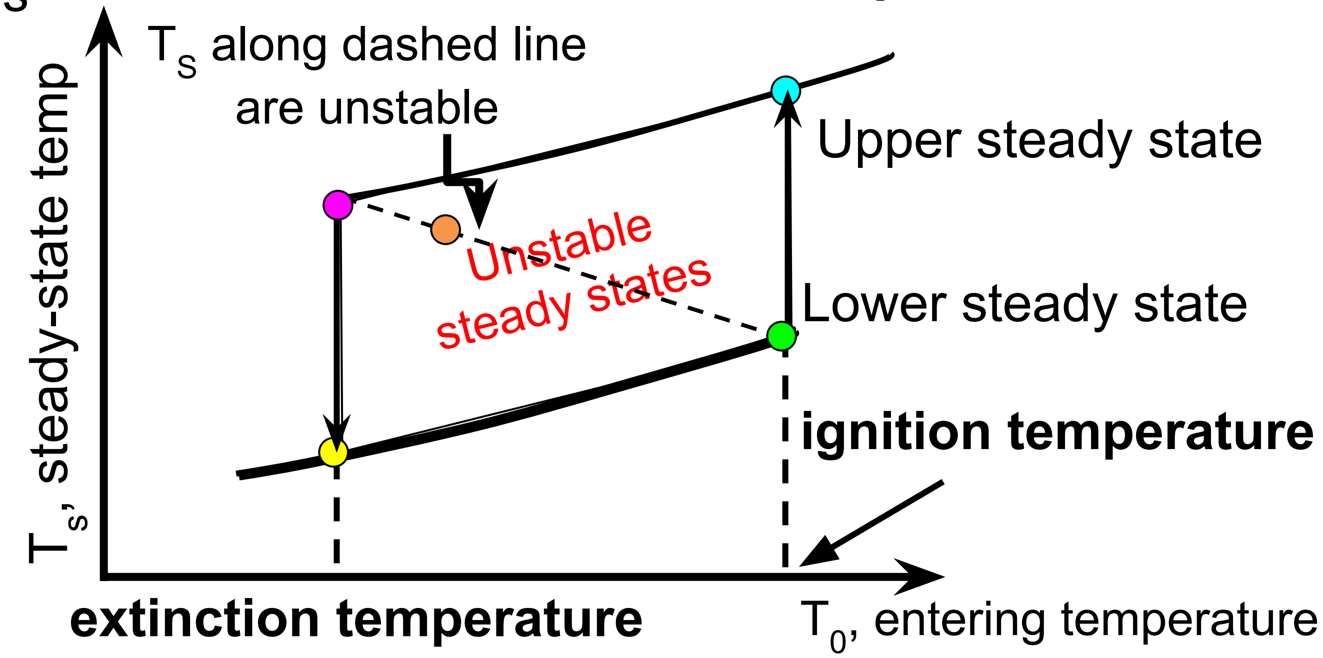
Temperature Ignition-Extinction Curve

- Slight increase in T above $T_{S,green}$ causes reactor T to jump to $T_{S,cyan}$
- Ignition temp: T where jump from $T_{S,lower}$ to $T_{S,upper}$ occurs
- Slight decrease in T below $T_{S,magenta}$ causes reactor T to drop to $T_{S,yellow}$
- Extinction temp: T where drop from $T_{S,upper}$ to $T_{S,lower}$ occurs

Plot T_S vs T_0





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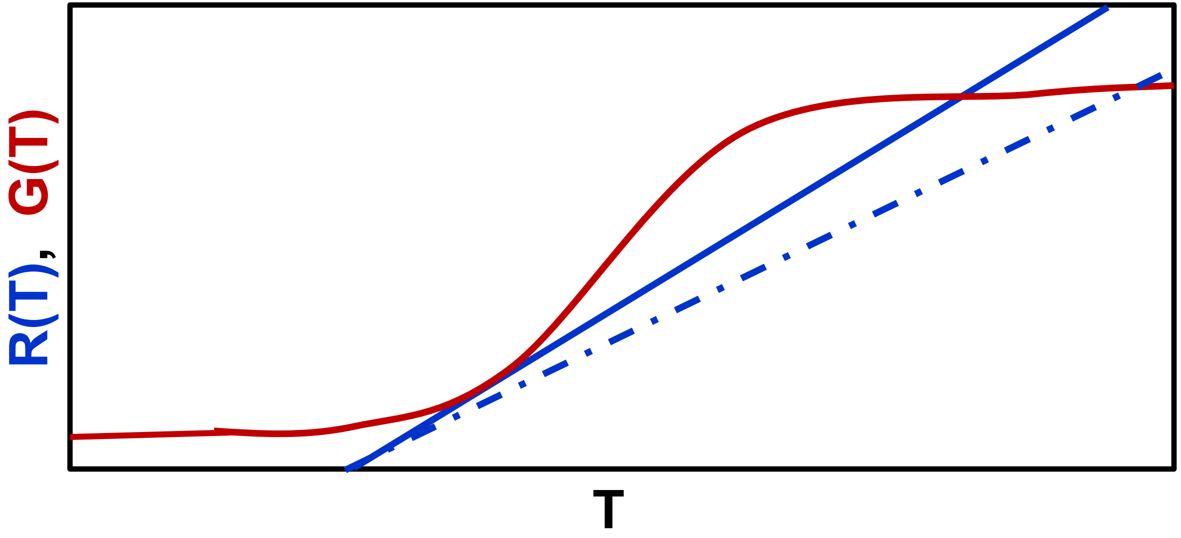
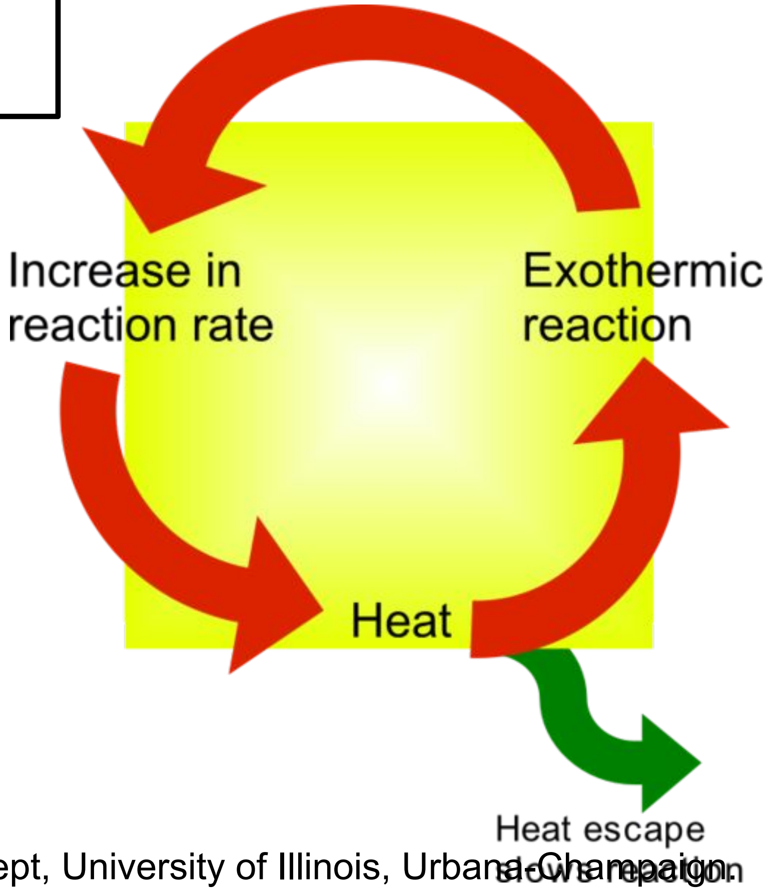
Runaway Reaction



Ignition temperature is very important: once T_0 exceeds $T_{ignition}$, transition to the upper steady state will occur

- undesirable
- dangerous

Runaway reaction
R(T) only intersects with upper steady state



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