ChE 344
Reaction Engineering and Design

Lecture 18: Thurs, Mar 17, 2022

Non-isothermal examples

Reading for today's Lecture: Chapter 12.3, 12.6

Reading for Lecture 19: Chapter 13

Lecture 18: Non-isothermal Reactor Design-CSTR with heat exchangers + multiple reactions
Related Text: Chapter 12.3, 12.6

Algorithm for solving CSTRs with heat effects with conversion.

If temperature is specified in the problem (recall assumptions necessary):

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

If conversion is specified in the problem:

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

Once you have both T and X, you can solve for the reactor volume using the mole balance equation for a CSTR:

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

If reactor volume is specified in the problem you will need to plot R(T) and G(T) and find intersections, as there may be multiple steady states.

For CSTR with multiple reactions:

Cannot solve with conversion so need mole balance for each individual species. For the energy balance below:

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

The first term is positive if $T_0 > T$ (feed in is heating up the reactor contents), the third term is positive if $T_a > T$ (heat exchanger fluid is heating the reactor contents). The middle term is positive if the reaction rate of species j is negative and the heat of reaction is negative (exothermic). The middle term is our generation of heat, and the first and last terms are our removal of heat (combined into one for CSTR, as heat can be changed without reaction either by a heat exchanger or by the feed in being different temperature than the reactor/outlet temperature). For large coolant flow rate you may use (see Lecture 17 summary for definitions):

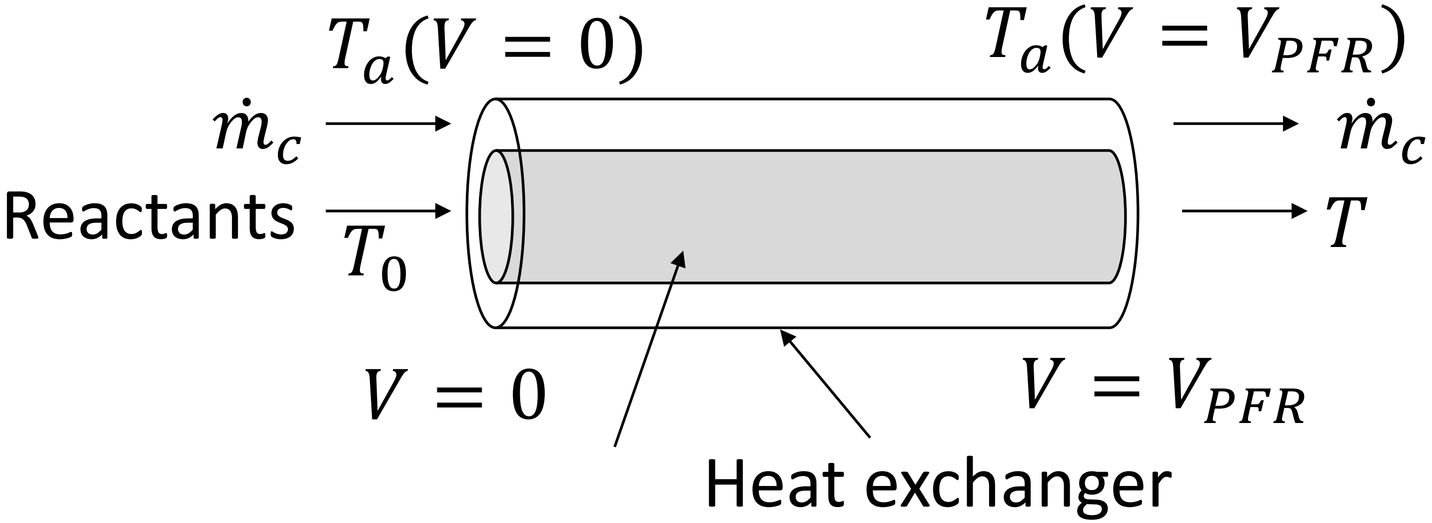
$$R(T) = C_{P0}(1+\kappa)(T-T_c)$$

$$G(T) = \frac{V}{F_{A0}}\sum_{i=1}^{n} r_{ij}\Delta H_{rxn,ij}$$

Example for two reactions:

$$G(T) = \frac{\tau}{C_{A0}}\left(-k_1 C_A \Delta H_{rxn,1A} - k_2 C_B \Delta H_{rxn,\,2B}\right)$$

Review of PFR/PBR with heat exchanger:



Mole balance

$$\frac{dF_j}{dV} = r_j$$

Energy balance

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

Co-current E.B.

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

Counter current E.B.

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

CSTR algorithm(s) recall assumptions, see L17 and summary

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

T specified

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

X specified

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

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

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

How can we think of κ? Ratio of heat transfer from 'coolant' to total heat capacity in from inlet flow for our system

$$\kappa \equiv \frac{UA}{F_{A0} C_{P0}}$$

UA [=] $\text{J}\ \cancel{\text{m}^{-2}}\ \text{s}^{-1}\ \text{K}^{-1} * \cancel{\text{m}^{2}}$

Lecture 16

$F_{A0} C_{P0}$ [=] $\cancel{\text{mol}}\ \text{s}^{-1} * \text{J}\ \cancel{\text{mol}^{-1}}\ \text{K}^{-1}$

How can we think of T_c? Relevant temp to use when considering our gradient from the reactor temp T

$$T_c \equiv \frac{\kappa T_a + T_0}{1 + \kappa}$$

Weighting T_0 and T_a

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

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

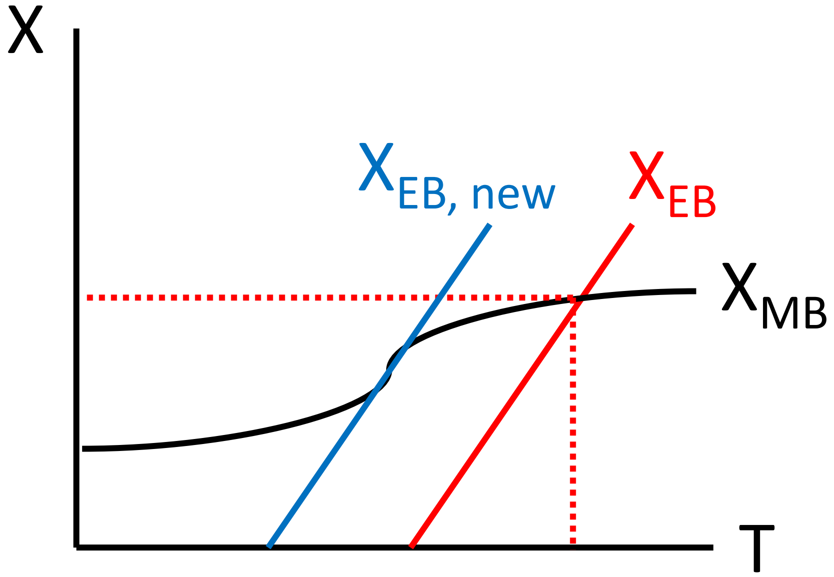
$$C_{P0}(1 + \kappa)(T - T_c)$$

Heat is removed due to this gradient

If volume of CSTR is 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 X_{EB} and X_{MB} vs. T and find intersections



Caution! There may be multiple steady states, and so if you don’t graphically look at the plot you may miss some solutions! To avoid, use G(T) and R(T) and find steady states.

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 for multiple rxns:

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

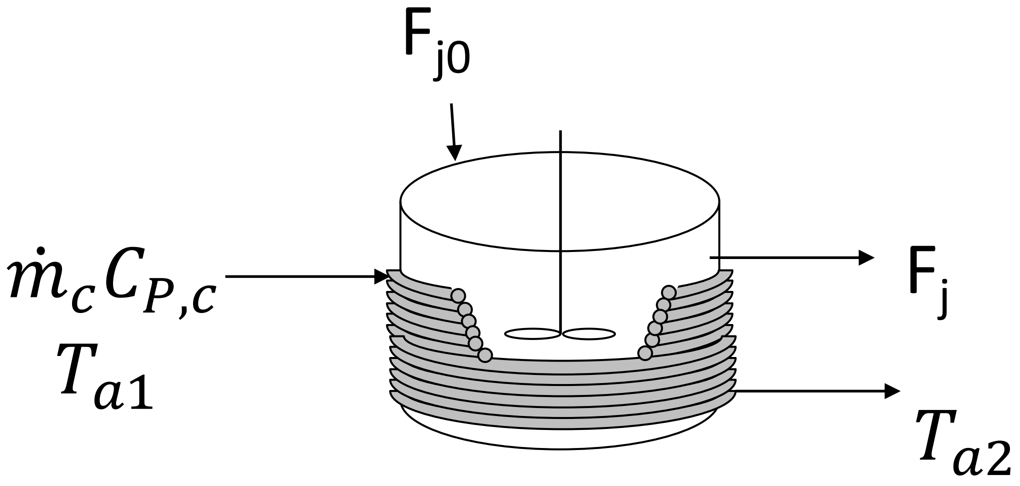
CSTR multiple reactions

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

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.

CSTR with multiple reactions, assuming all inlet flows are the same $T=T_0$, no shaft work, steady state, large coolant flow rates ($T_{a1}=T_{a2}$), no change in PE, KE (recall those assumptions from adiabatic E.B.)



Number of rxns

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

Today: Going through examples

P**B**R reversible reaction with co-current heat exchanger (LEP T12-2)

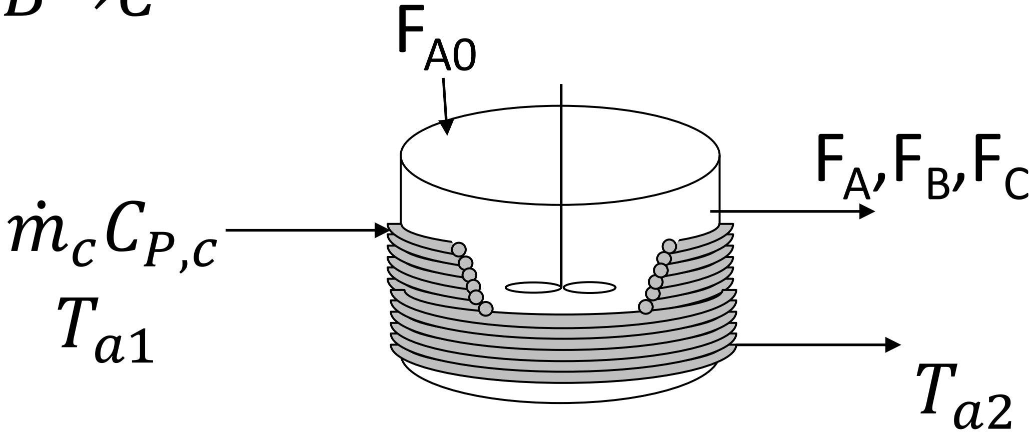
$$A + B \rightleftarrows 2C$$

ρ_b = bed density

CSTR with multiple reactions and heat exchanger (LEP 12-6)

$$A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$

Assuming in this example T_{a1} = T_{a2}



Elementary gas-phase reaction (Chap 12.3)

$$A + B \rightleftarrows 2C$$

In a packed bed reactor with inert and with co-current heat exchanger

Mole balance:

$$\frac{dX}{dW} = \frac{-r_A'}{F_{A0}}$$

Rate law:

$$-r_A' = k_1\left(C_A C_B - \frac{C_C^2}{K_C}\right)$$

$$k_1 = k_1(T_1)\exp\left(\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$$

$If\ \Delta C_P = 0$

$$K_C = K_C(T_2)\exp\left(\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right)$$

Stoichiometry (gas-phase):

$$C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}\frac{T_0}{T}p$$

$$\varepsilon = y_{A0}\delta = \frac{1}{3}(2-1-1) = 0$$

$$C_A = C_{A0}(1-X)\frac{T_0}{T}p$$

$$C_B = C_{A0}(\theta_B - X)\frac{T_0}{T}p$$

$$C_C = C_{A0}(2X)\frac{T_0}{T}p$$

$$C_I = C_{I0}\frac{T_0}{T}p$$

Ergun Equation:

$$\frac{dp}{dW} = \frac{-\alpha}{2p}(1 + \varepsilon X)\frac{T}{T_0}$$

$$\frac{dp}{dW} = \frac{-\alpha}{2p}\frac{T}{T_0}$$

Combine (gas-phase):

$$-r_A' = k_1\left(C_A C_B - \frac{C_C^2}{K_C}\right)$$

$$-r_A' = k_1 C_{A0}^2\left((1 - X)(\theta_B - X) - \frac{(2X)^2}{K_C}\right)\left(\frac{T_0}{T}p\right)^2$$

At equilibrium, $-r_A' = 0, X = X_{eq}$

$$X_{eq} = \frac{(\theta_B + 1)K_C - \left[\left((\theta_B + 1)K_C\right)^2 - 4K_C\theta_B(K_C - 4)\right]^{1/2}}{2(K_C - 4)}$$

Energy balances:

Q_g' Q_r'

On reactor:

$$\frac{dT}{dW} = \frac{r_A' \Delta H_{rxn} - \left(\frac{Ua}{\rho_b}\right)(T - T_a)}{\sum F_i C_{P,i}} = \frac{Q_g' - Q_r'}{\sum F_i C_{P,i}}$$

$$\sum F_i C_{P,i} = F_{A0}\left[C_{P,A} + \theta_B C_{P,B} + \boldsymbol{\theta_I C_{P,I}} + X \Delta C_P\right]$$

On co-current coolant:

$$\frac{dT_a}{dW} = \frac{\left(\frac{Ua}{\rho_b}\right)(T - T_a)}{\dot{m}_c C_{P,coolant}}$$

Mole balances using molar flow rates:

$$\frac{dF_A}{dW} = r'_A \qquad \frac{dF_B}{dW} = r'_B \qquad \frac{dF_C}{dW} = r'_C$$

$$F_I = F_{I0}$$

Rate law:

$$-r'_A = k_1\left(C_A C_B - \frac{C_C^2}{K_C}\right)$$

Stoichiometry (gas-phase):

$$r'_A = r'_B$$

$$-2r'_A = r'_C$$

Stoichiometry (gas-phase):

$$C_A = C_{T0}\frac{F_A}{F_T}\frac{T_0}{T}p$$

$$C_B = C_{T0}\frac{F_B}{F_T}\frac{T_0}{T}p$$

$$C_C = C_{T0}\frac{F_C}{F_T}\frac{T_0}{T}p$$

$$F_T = F_A + F_B + F_C + F_I$$

$$\frac{dp}{dW} = \frac{-\alpha}{2p}\frac{F_T}{F_{T0}}\frac{T}{T_0}$$

Using parameters in Living Example Problem T12-2

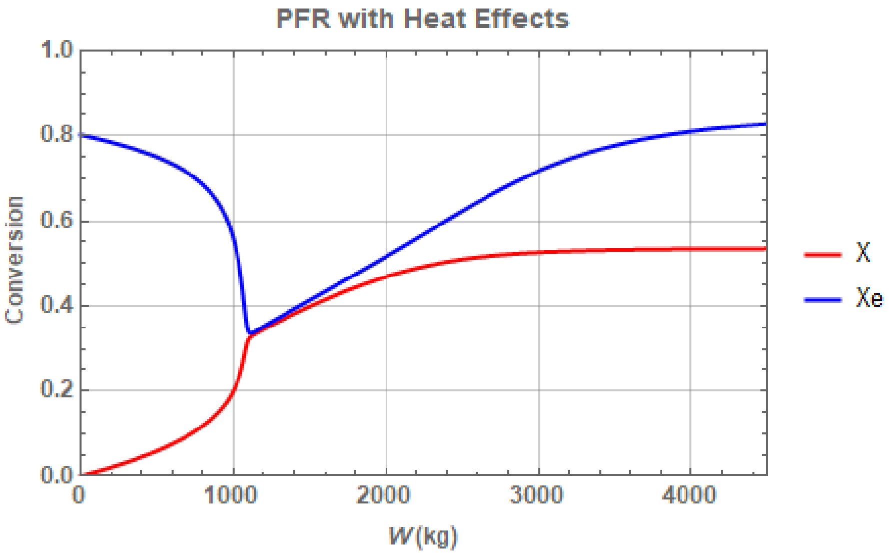
$$\frac{dT_a}{dW} = \frac{\left(\frac{Ua}{\rho_b}\right)(T - T_a)}{\dot{m}_c C_{P,coolant}}$$

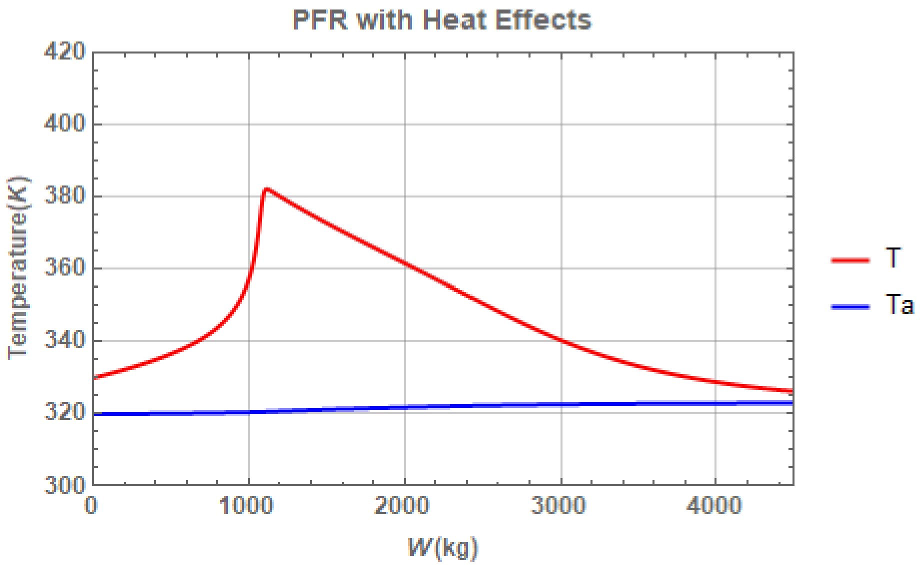
$$\frac{dp}{dW} = \frac{-\alpha}{2p}\frac{T}{T_0}$$

$$\frac{dT}{dW} = \frac{Q'_g - Q'_r}{\sum F_i C_{P,i}}$$

$$\frac{dX}{dW} = \frac{-r'_A}{F_{A0}}$$

Plus other eqns for K$_C$, r'_A, etc.



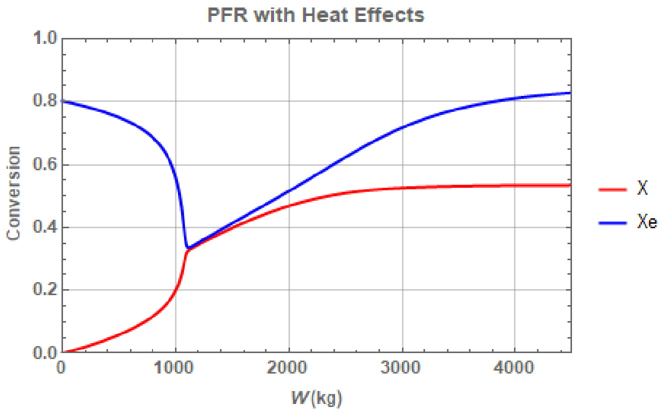


Discuss with your neighbors:

Which PBR has the highest heat exchange (Ua)?

Is that the ideal reactor condition for X?

A)



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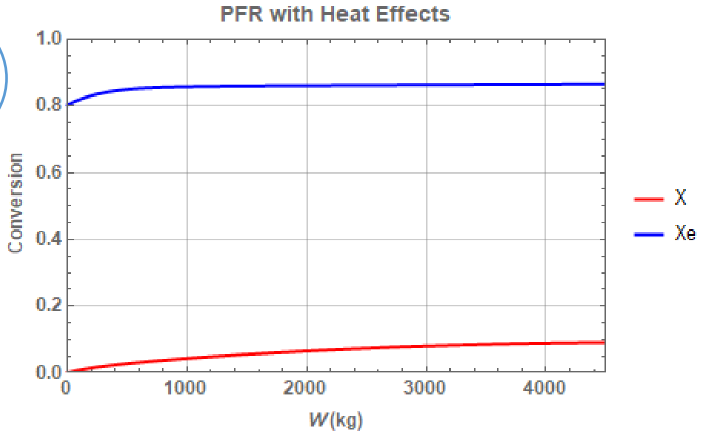

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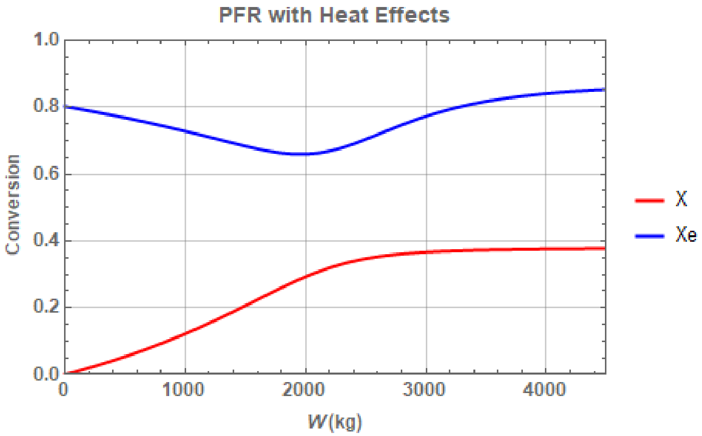

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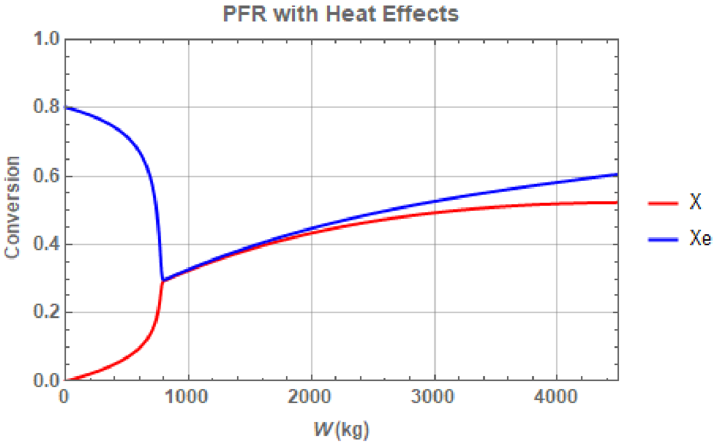


Next example: CSTR (liquid phase) 12-6

$\boxed{V = 10\text{ L};}$ v_0 = 1000 L/min; C_{A0} = 0.3 mol/L; T_0 = 283 K; $\tau = \frac{10}{1000}$

Heat capacity

$C_{P,A} = C_{P,B} = C_{P,C}$ = 200 J/mol·K ($\Delta C_P = 0$)

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Kinetics

k_1(300 K) = 3.3 1/min; k_2(500 K) = 4.58 1/min;

E_{a1} = 9900 cal/mol; E_{a2} = 27000 cal/mol;

Thermodynamics

$\Delta H_{rxn,1A}$=-55 kJ/mol; $\Delta H_{rxn,2B}$= -71.5 kJ/mol;

Heat Exchanger

UA= 40000 J/min·K; T_a= 57 °C (330 K) Assume constant T_a

Qs: What is the outlet concentration, are there multiple steady states, and are they stable?

Start with reaction rate laws:

$$r_{1A} = -k_1 C_A = -r_{1B}$$

$$r_{2B} = -k_2 C_B$$

$$r_A = -k_1 C_A$$

$$r_B = k_1 C_A - k_2 C_B$$

Mole balance for A in a CSTR (not in terms of conversion):

$$V = \frac{F_{A0} - F_A}{-r_A} = \frac{v_0 (C_{A0} - C_A)}{k_1 C_A}$$

$$\frac{V}{v_0} = \tau = \frac{C_{A0} - C_A}{k_1 C_A} \rightarrow C_A = \frac{C_{A0}}{1 + k_1 \tau}$$

Mole balance for B in a CSTR:

$$V = \frac{F_{B0} - F_B}{-r_B} = \frac{v_0(C_{B0} - C_B)}{-k_1 C_A + k_2 C_B}$$

$$\frac{V}{v_0} = \tau = \frac{C_{B0} - C_B}{-k_1 C_A + k_2 C_B} \rightarrow C_{B0} - C_B = \tau(-k_1 C_A + k_2 C_B)$$

$$C_{B0} + \tau k_1 C_A = C_B(1 + k_2 \tau)$$

$$\frac{C_{B0} + \tau k_1 C_A}{1 + k_2 \tau} = C_B$$

$$C_B = \frac{\cancel{C_{B0}} + \tau k_1 C_A}{1 + k_2 \tau} = \frac{\tau k_1 C_{A0}}{(1 + k_2 \tau)(1 + k_1 \tau)}$$

Energy balance:

Positive if $T_a > T$

Negative if $T_a < T$

Positive if $T_0 > T$

Negative if $T_0 < T$

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

$$C_{P0}(1 + \kappa)(T - T_c) = \frac{V}{F_{A0}} \sum_{i=1}^{n} r_{ij} \Delta H_{rxn,ij}$$

$$C_{P0} = \sum \theta_i C_{P,i} = \theta_A C_{P,A} + \theta_B C_{P,B} + \theta_C C_{P,C} = C_{P,A}$$

Two terms from three because recall the reactor effluent removing heat is also like a heat exchanger and is part of T_c.

$$\sum_{i=1}^{n} r_{ij}\Delta H_{rxn,ij} = r_{1A}\Delta H_{rxn,1A} + r_{2B}\Delta H_{rxn,2B}$$

Units:

(mol A L^{-1} s^{-1})(kJ [mol A]$^{-1}$) (mol B L^{-1} s^{-1})(kJ [mol B]$^{-1}$)

Species *j* is switching (no A in rxn 2), between sums

*Note $r_{1A}\Delta H_{rxn,1A}$ is positive if A is being consumed in rxn 1 and the reaction is exothermic (makes sense in E.B.)

$$\sum_{i=1}^{n} r_{ij}\Delta H_{rxn,ij} = -k_1 C_A \Delta H_{rxn,1A} - k_2 C_B \Delta H_{rxn,2B}$$

$$= -k_1 \frac{C_{A0}}{1+k_1\tau}\Delta H_{rxn,1A} - k_2 \frac{\tau k_1 C_{A0}}{(1+k_2\tau)(1+k_1\tau)}\Delta H_{rxn,2B}$$

$$\kappa \equiv \frac{UA}{F_{A0}C_{P0}} = 0.667$$

$$T_c \equiv \frac{\kappa T_a + T_0}{1+\kappa} = 301.8K$$

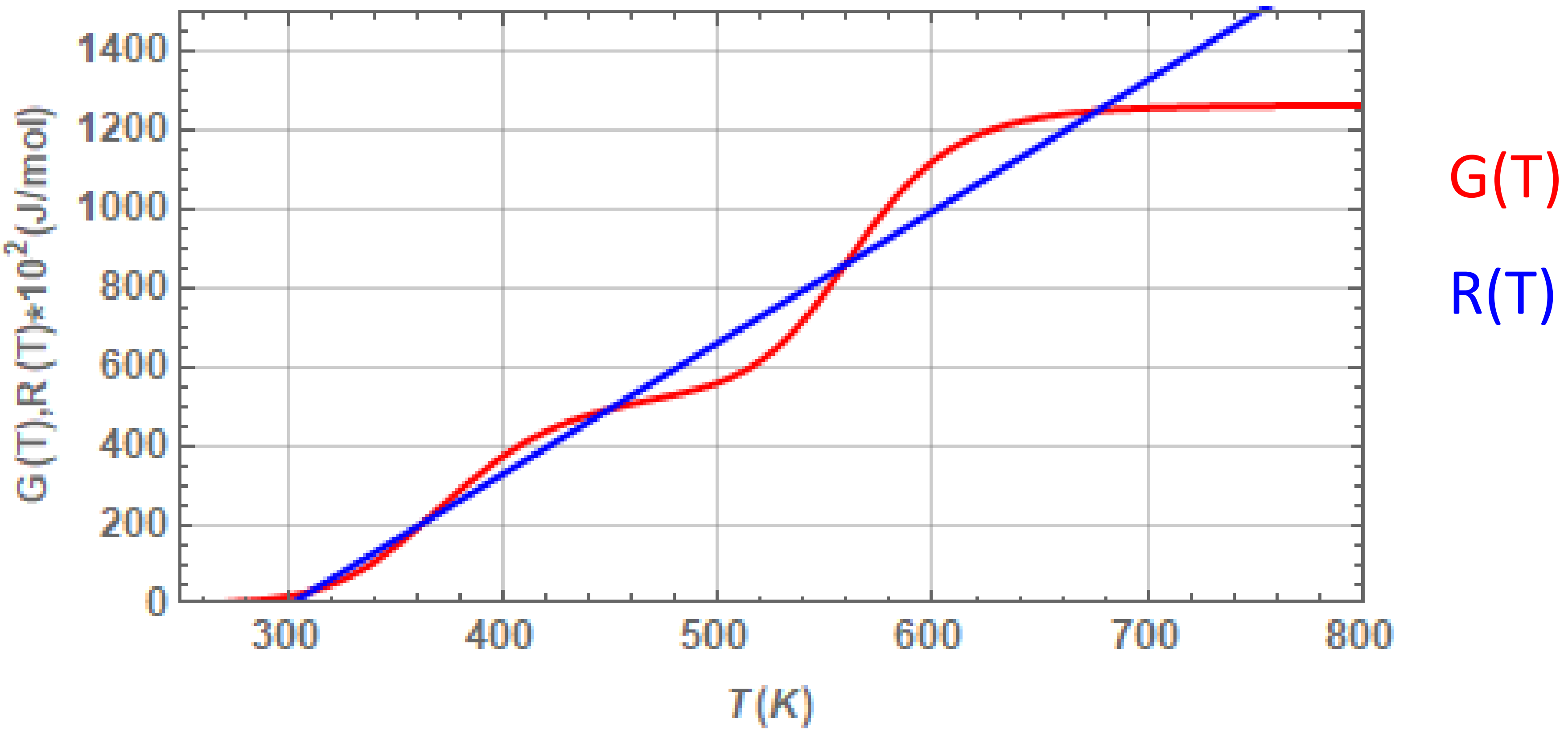
$$C_{P0} = C_{P,A} = 200\, J/mol \cdot K$$

$$\boxed{R(T) = C_{P0}(1+\kappa)(T-T_c)}$$

$$\boxed{G(T) = \frac{V}{F_{A0}}\sum_{i=1}^{n} r_{ij}\Delta H_{rxn,ij} = \frac{\tau}{C_{A0}}\left(-k_1 C_A \Delta H_{rxn,1A} - k_2 C_B \Delta H_{rxn,2B}\right)}$$

Discuss with your neighbors:

How many stable steady states are there for these conditions for the multiple reactions CSTR we solved for?



A) 5

[✓ B) 3]

C) 2

D) No stable steady states