A First Course on Kinetics and Reaction Engineering

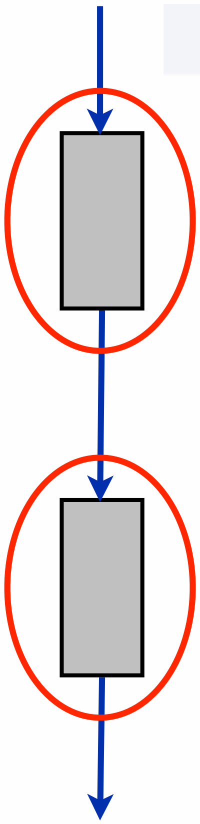
Class 31 on Unit 29

Where We're Going

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
- Part III - Chemical Reaction Engineering
  - A. Ideal Reactors
  - B. Perfectly Mixed Batch Reactors
  - C. Continuous Flow Stirred Tank Reactors
  - D. Plug Flow Reactors
  - E. Matching Reactors to Reactions
    - 28. Choosing a Reactor Type
    - 29. Multiple Reactor Networks
    - 30. Thermal Back-Mixing in a PFR
    - 31. Back-Mixing in a PFR via Recycle
    - 32. Ideal Semi-Batch Reactors
- Part IV - Non-Ideal Reactions and Reactors

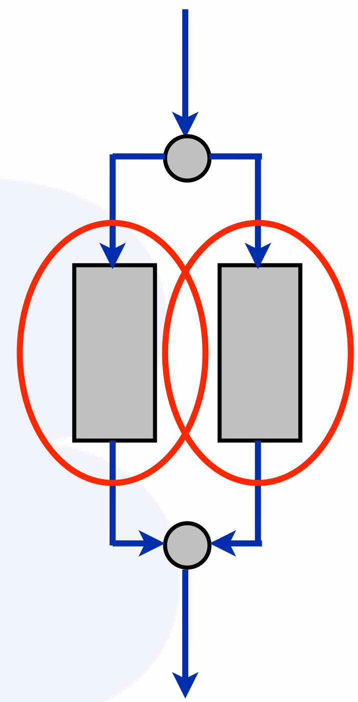
Reactor Networks

Series



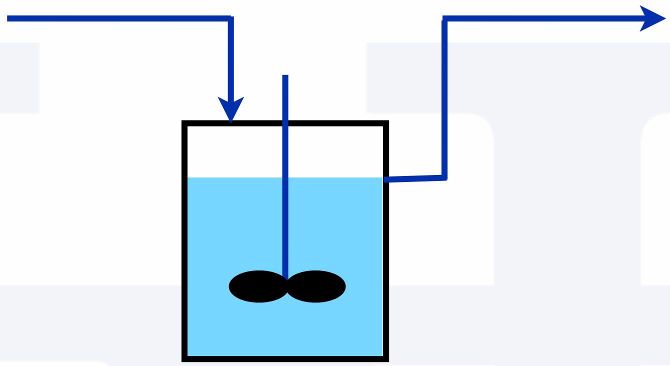
- Reasons for using multiple reactors
  - Add capacity to an existing process
  - Performance Advantages
    - Heat management
    - More favorable composition vs. space time
- No difference in model for an individual reactor
  - Equations may become coupled with those for another reactor
  - May need additional mole and energy balances at splitting and mixing points
- General behavior
  - Two PFRs (of equal diameter) connected in series are equivalent to a single PFR with their combined length provided no heating, cooling or fluid exchange takes place between them
  - Mixing two streams of unequal conversion generally decreases the performance of a parallel reactor network compared to networks where such mixing does not occur
- CSTR cascades (CSTRs in series)
  - As the number of CSTRs in the cascade increases, keeping total volume constant, the cascade performs more and more like a PFR

Parallel



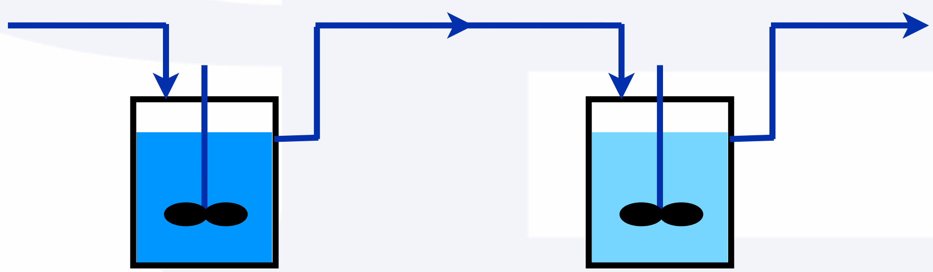
Advantage of a CSTR Cascade over a Single CSTR

Inlet composition and temperatures are equal



Outlet composition and temperatures are equal

Rates are Equal



Rate is Higher

Since some of the reaction occurs at a higher rate with 2 reactors the total volume is smaller

Solving Reactor Network Problems

- Read through the problem statement and make a sketch of the network in which each flow stream, reactor, stream split and stream merge is labeled
- Read through the problem statement a second time and (a) assign each quantity given in the problem statement to the appropriate variable symbol (b) choose a basis, if necessary and (c) determine what quantities the problem asks for and assign appropriate variable symbols to them
- Write the design equations for each reactor in the network
- If the design equations for any of the individual reactors can be solved at this point, do so and then repeat this step
- Write mole and energy balances for each stream split and for each stream merge and solve any that can be solved
- If the design equations for any of the individual reactors can be solved at this point, do so and then repeat this step
- Solve all of the remaining equations simultaneously or, if possible, group them into sets that can be solved independently and solve each set
- After the all of the equations have been solved, use the results to calculate any other quantities or make any plots that the problem asked for

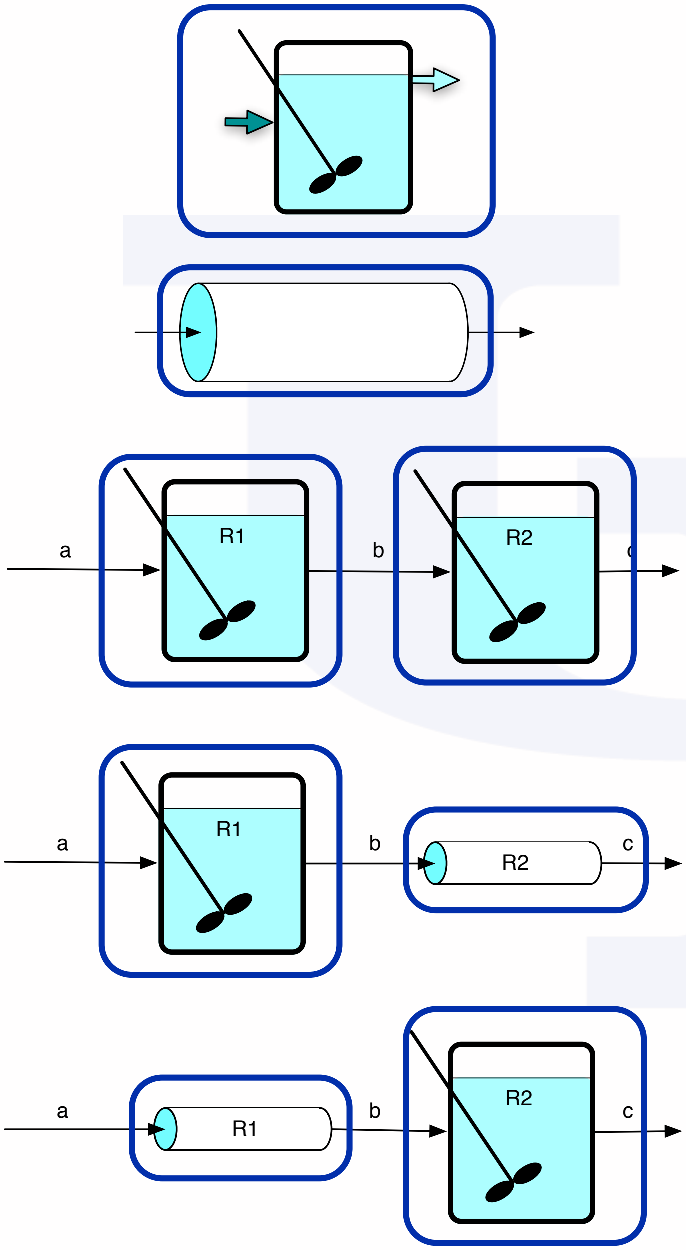
Questions?

Activity 29

Consider the irreversible, liquid phase reaction A → B which occurs at constant density. Reactant A is supplied at a rate of 4 L min^{-1} in a concentration of 2 mol L^{-1} and at a temperature of 43 ºC. The heat capacity of the fluid is 0.87 cal mL^{-1} K^{-1} and the heat of reaction is -27.2 kcal mol^{-1}. The reaction is second order in the concentration of A, and the rate coefficient obeys Arrhenius' law with a pre-exponential factor of 6.37 x 10^9 L mol^{-1} min^{-1} and an activation energy of 14.3 kcal mol^{-1}. It is desired to convert 90% of the reactant to product adiabatically. Consider the following reactor networks: (a) a single CSTR, (b) a single PFR, (c) two CSTRs in series, (d) a CSTR followed in series by a PFR, and (e) a PFR followed in series by a CSTR. Determine which reactor network requires the smallest total reactor volume. (In each of the reactor networks, the two reactors are *not* required to have equal volumes.)

Read through the problem statement and make a sketch of the network in which each flow stream, reactor, stream split and stream merge is labeled

Reactor Networks



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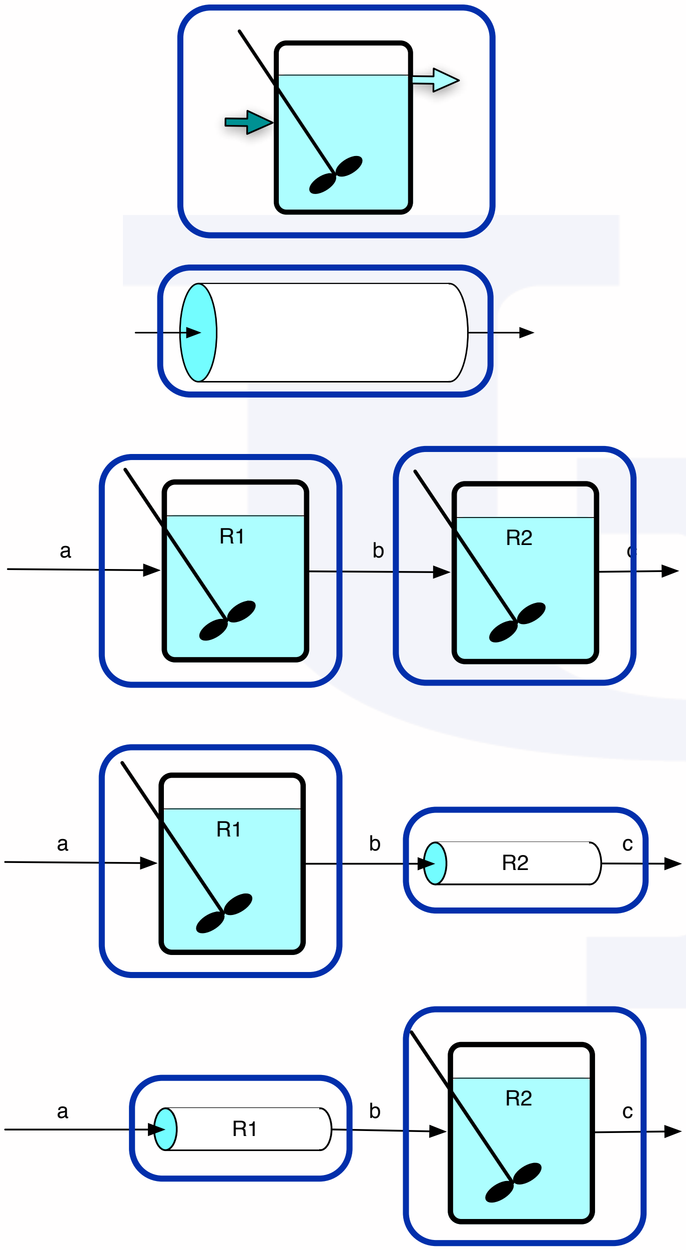
Reactor Networks



- Given: $\dot{V}^0 = 4$ L min^{-1}, $C_A^0 = 2$ mol L^{-1}, $T^0 = (43 + 273.15)$ K, $C_p = 0.87$ 0.87 cal mL^{-1} K^{-1}, $\Delta H(T) = -27.2$ kcal mol^{-1}, $k_0 = 6.37 \times 10^9$ L mol^{-1} min^{-1}, E = 14.3 kcal mol^{-1} and $f_{A,final} = 0.9$
-

Design Equations

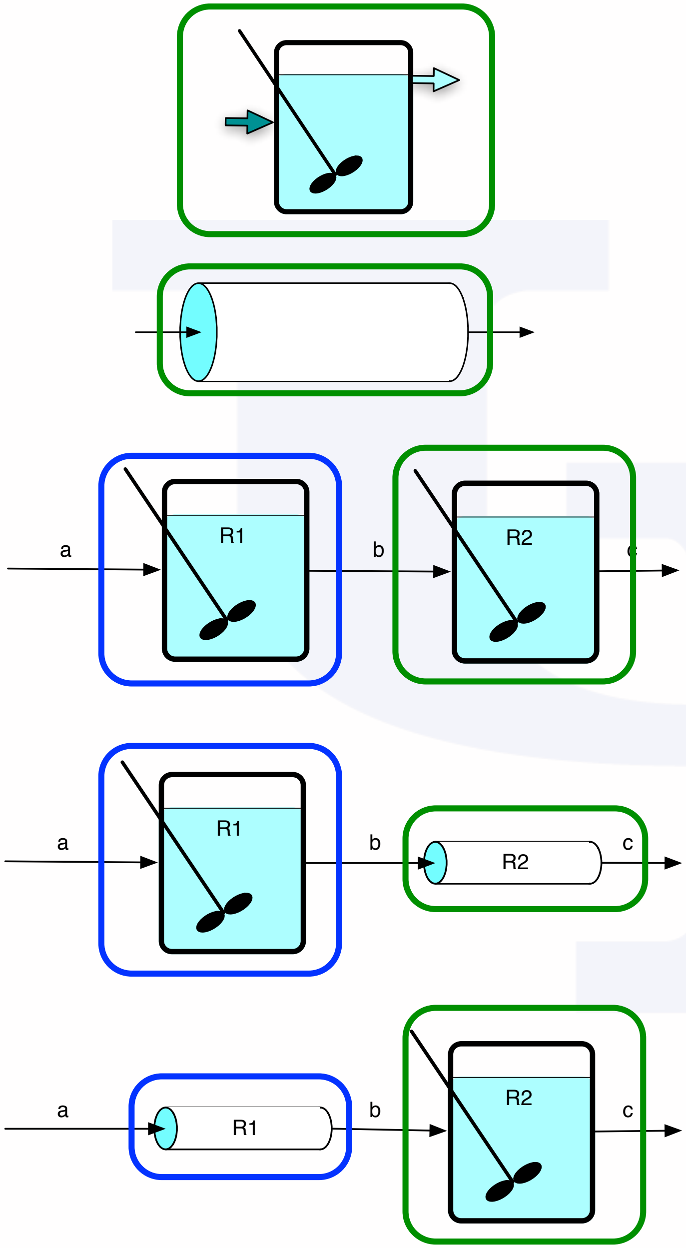
- Write design equations that can be used to analyze any of the CSTRs
- Write design equations that can be used to analyze any of the PFRs

Design Equations

- Write design equations that can be used to analyze any of the CSTRs
  - $0 = \dot{n}_{A,in} - \dot{n}_{A,out} - Vr_{out}$
  - $0 = \dot{n}_{B,in} - \dot{n}_{B,out} + Vr_{out}$
  - $0 = \dot{V}_{in}\tilde{C}_p\left(T_{out} - T_{in}\right) + Vr_{out}\Delta H\left(T_{out}\right)$
    - $r_{out} = k_0 \exp\left(\frac{-E}{RT_{out}}\right)C_{A,out}^2$
  - 3 equations, so 3 unknowns
    - $\dot{n}_{B,out}$ and T_{out} in all cases
    - $\dot{n}_{A,out}$ when CSTR is the first reactor
    - V when CSTR is the second or the only reactor

- Write design equations that can be used to analyze any of the PFRs
  - $\frac{d\dot{n}_A}{dV} = -r; \quad \dot{n}_A\left(0\right) = \dot{n}_{A,in}$
  - $\frac{d\dot{n}_B}{dV} = r; \quad \dot{n}_B\left(0\right) = \dot{n}_{B,in}$
  - $\frac{dT}{dV} = \frac{-r\Delta H\left(T\right)}{\dot{V}\tilde{C}_p}; \quad T\left(0\right) = T_{in}$
    - $r_{out} = k_0 \exp\left(\frac{-E}{RT}\right)C_A^2$
  - Final condition
    - V when PFR is the first reactor
    - $\dot{n}_{A,out}$ when PFR is the second reactor

Individual Reactors



- For every CSTR
  - Design equations from previous slide
  - $\dot{n}_{B,out}$ and T_{out} are unknown
- For first CSTR if there are 2 reactors
  - $\dot{n}_{A,out}$ is unknown
- For last CSTR
  - V is unknown
- For every PFR
  - Design equations and initial conditions from previous slide
- For first PFR if there are 2 reactors
  - Final value is V
- For last PFR
  - Final value is $\dot{n}_{A,out}$

Numerical Solution

- For the single reactors, simply solve the design equations to find V
- For each reactor network
  - Pick a range of values for the first reactor volume between zero and the volume of the single reactor found above
  - For each volume in that range
    - Solve the design equations for the first reactor to get molar flow rates of A and B and temperature for stream b in diagrams
    - Use those results to solve the design equations for the second reactor to get its volume
    - Calculate the total volume and plot it versus the volume of the first reactor
  - Find the minimum in the plot and from it, read the minimum volume for that reactor network
- Solving the CSTR design equations requires a guess for the solution
  - It may be difficult or impossible to find a single guess that works over the whole range of volumes
    - Either solve over smaller ranges of volume
    - Or write the code so the guesses are varied appropriately

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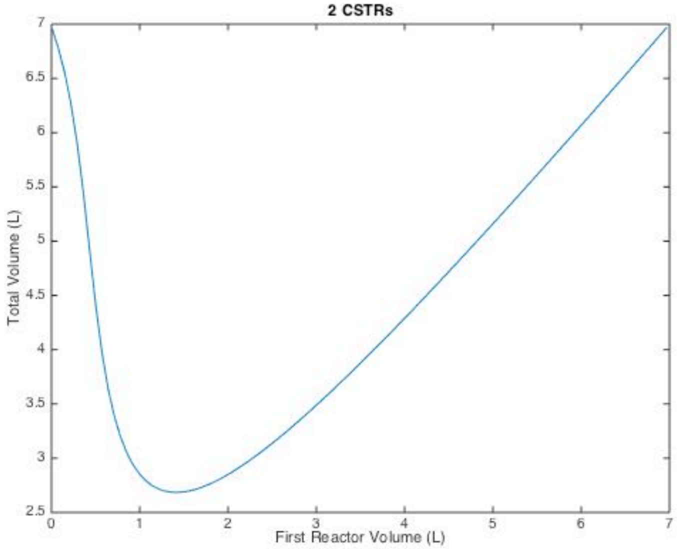
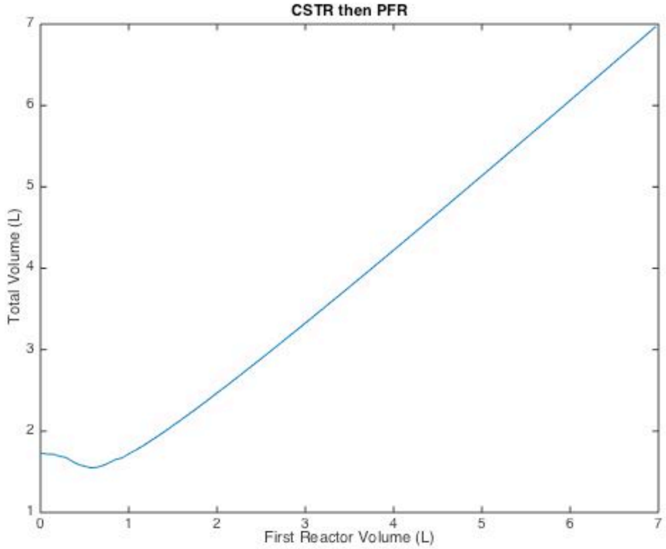
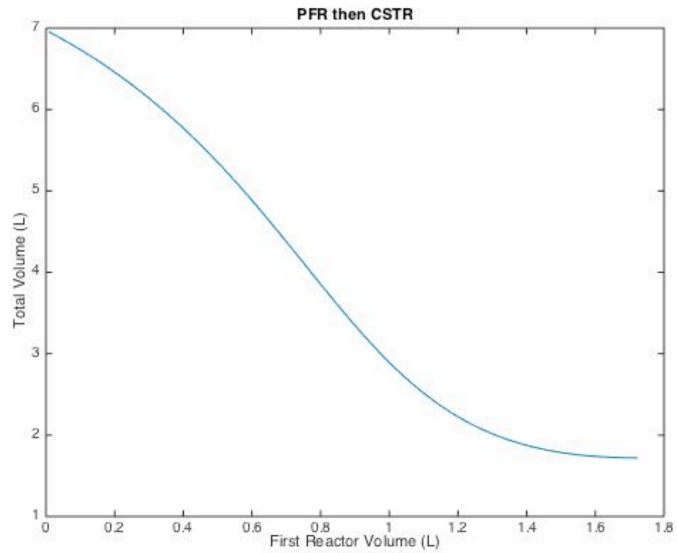
    - Or write the code so the guesses are varied appropriately
- Results from smallest to largest
  - Single CSTR (7.0 L) > 2 CSTRs (2.7 L) > single PFR = PFR before CSTR (1.7 L) > CSTR before PFR (1.5 L)

Volume Plots







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