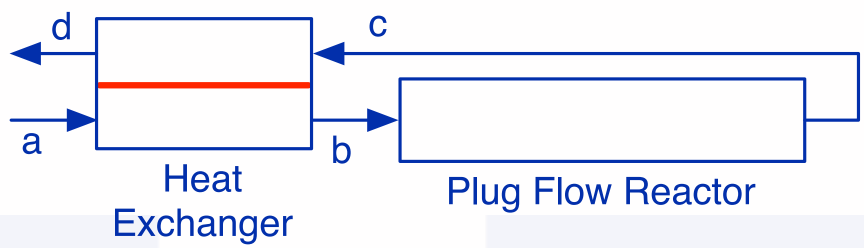
A First Course on Kinetics and Reaction Engineering

Class 32 on Unit 30

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

Thermal Back-Mixing of a PFR



- The PFR design equations are the same as a stand-alone PFR
  - Often you can't solve them independently because the inlet temperature, T_b, is not specified
- Design equations for the heat exchanger
  - Energy balance
    - $$\sum_{\substack{i=all\\species}} \dot{n}_{i,c} \int_{T_c}^{T_d} \hat{C}_{p,i}\, dT + \sum_{\substack{i=all\\species}} \dot{n}_{i,a} \int_{T_a}^{T_b} \hat{C}_{p,i}\, dT = 0$$
  - Heat transfer equation (one of the following)
    - $$\sum_{\substack{i=all\\species}} \dot{n}_{i,c} \int_{T_c}^{T_d} \hat{C}_{p,i}\, dT + UA\Delta T_M = 0$$
      - $$\Delta T_{LM} = \frac{\left(T_d - T_a\right) - \left(T_c - T_b\right)}{\ln\left\{\frac{\left(T_d - T_a\right)}{\left(T_c - T_d\right)}\right\}}$$
      - $$\Delta T_{AM} = \frac{T_c + T_d}{2} - \frac{T_a + T_b}{2}$$
    - $$\Delta T_{cold} = T_d - T_a$$

Analysis of an Integrated Heat Exchanger and PFR

- Make a simple schematic and label each of the streams
- Assign each quantity that is specified in the problem statement to the appropriate variable
- Set up the design equations for the PFR
    - If there is sufficient information to solve the PFR design equations
        - Solve the PFR design equations
        - Use the results to solve the heat exchanger design equations
    - If the PFR design equations cannot be solved independently
        - Set up the two design equations for the heat exchanger
        - In preparation for solving the heat exchanger design equations numerically, choose T_b as one of the unknowns and _do not_ choose T_c or any molar flow rate as the other unknown
        - Solve the heat exchanger design equations numerically
            - The code you must provide will be given T_b
                - knowing that, you can solve the PFR design equations to obtain T_c and any unknown molar flow rates
                - knowing those, you can evaluate the heat exchanger design equations
        - Once the heat exchanger design equations are solved, use the results to solve the PFR design equations
- Answer the questions posed in the problem statement

Questions?

An acid, A, is to be hydrolyzed according to the reaction A + W → P, where W represents water and P, the product. The acid will be fed to an adiabatic, steady state PFR at 0.07 kmol/s and water will be fed at 1.67 kmol/s. This gives a total feed flow of 0.04 m^3/s. The feed temperature is 300 K. The fluid volume of the PFR is 0.5 m^3. The rate expression is given in equation (1), with the rate coefficient given in equation (2) and the equilibrium constant in equation (3). The heat of reaction is -86,000 kJ/kmole at 298 K. The heat capacities of A, W, and P are 412, 76, and 512 kJ/(kmol K), respectively, and may be taken to be independent of temperature. Compare the conversions and final temperatures when (a) the feed enters the PFR directly and (b) when the product stream is used to heat the feed (assume a 5 K cold approach).

$$r_1 = kC_AC_W\left[1-\frac{C_P}{KC_AC_W}\right] \quad (1)$$

$$k = \left(1.2\ \times\ 10^{12}\ \mathrm{m}^3\ \mathrm{kmol}^{-1}\ \mathrm{s}^{-1}\right)\exp\left\{\frac{-13000K}{T}\right\} \quad (2)$$

$$K = \left(4.2\ \times\ 10^{-15}\ \mathrm{m}^3\ \mathrm{kmol}^{-1}\right)\exp\left\{\frac{11300K}{T}\right\} \quad (3)$$

Activity 30.1

- In this activity you will practice the general approach for analyzing an integrated heat exchanger and PFR.
- It also illustrates a problem where the cold approach is specified and used as one of the heat exchanger design equations instead of the heat transfer equation
- Perform all work for this activity on the worksheet that has been provided

Sketch of the System

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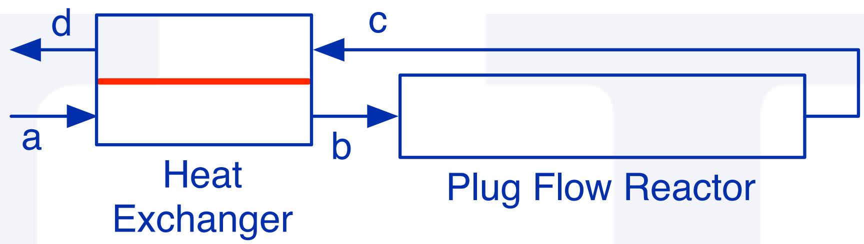

Identify Known Quantities

- Read through the problem statement. Each time you encounter a quantity, write it down and equate it to the appropriate variable. When you have completed doing so, if there are any additional constant quantities that you know will be needed and that can be calculated from the values you found, write the equations needed for doing so.

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  - $\dot{n}_{A,a}$ = 0.07 kmol s^{-1}
  - $\dot{n}_{W,a}$ = 1.67 kmol s^{-1}
  - $\dot{n}_{P,a}$ = 0.0 kmol s^{-1}
  - $\dot{V}_a$ = 0.04 m^3 s^{-1}
  - T_a = 300 K
  - V = 0.5 m^3
  - $k(T)$; k_0 = 1.2 x 10^{12} m^3 kmol^{-1} s^{-1}; E/R = 13000 K
  - $K(T)$: K_0 = 4.2 x 10^{-15} m^3 kmol^{-1}; $\Delta H/R$ = −11300 K
  - ΔH^0(298 K) = -86,000 kJ kmol^{-1}
  - $\tilde{C}_{p,A}$ = 412 kJ kmol^{-1} K^{-1}
  - $\tilde{C}_{p,W}$ = 76 kJ kmol^{-1} K^{-1}
  - $\tilde{C}_{p,P}$ = 512 kJ kmol^{-1} K^{-1}
  - ΔT_{cold} = 5 K
  - $T_d = T_a + \Delta T_{cold}$
  - $\dot{V}_a = \dot{V}_b = \dot{V}_c = \dot{V}_d = \dot{V}$

PFR Design Equations

- Generate the design equations needed to model the PFR by simplification of the general PFR design equations found in Unit 17 or on the AFCoKaRE Exam Handout.

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$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4}\left[\left(\sum_{\substack{j=all\\reactions}} \nu_{i,j} r_j\right) - \frac{\partial}{\partial t}\left(\frac{\dot{n}_i}{\dot{V}}\right)\right]$$

$$\frac{d\dot{n}_A}{dV} = f_1\left(V,\dot{n}_A,\dot{n}_W,\dot{n}_P,T\right) = -r$$

$$\frac{d\dot{n}_W}{dV} = f_2\left(V,\dot{n}_A,\dot{n}_W,\dot{n}_P,T\right) = -r$$

$$\frac{d\dot{n}_P}{dV} = f_3\left(V,\dot{n}_A,\dot{n}_W,\dot{n}_P,T\right) = r$$

$$\pi DU\left(T_e - T\right) = \frac{\partial T}{\partial z}\left(\sum_{\substack{i=\text{all}\\\text{species}}} \dot{n}_i \hat{C}_{p-i}\right) + \frac{\pi D^2}{4}\left(\sum_{\substack{j=\text{all}\\\text{reactions}}} r_j \Delta H_j\right) + \frac{\pi D^2}{4}\left[\frac{\partial T}{\partial t}\left(\sum_{\substack{i=\text{all}\\\text{species}}} \frac{\dot{n}_i \hat{C}_{p-i}}{\dot{V}}\right) - \frac{\partial P}{\partial t}\right]$$

$$\frac{dT}{dV} = f_4\left(V,\dot{n}_A,\dot{n}_W,\dot{n}_P,T\right) = \frac{-r\Delta H^0\left(T\right)}{\dot{n}_A\hat{C}_{p,A} + \dot{n}_W\hat{C}_{p,W} + \dot{n}_P\hat{C}_{p,P}}$$

Numerical Solution of the PFR Design Equations

- Identify the specific set of equations that needs to be solved and within those equations identify the independent and dependent variables, if appropriate, and the unknown quantities to be found by solving the equations.

- Assuming that the PFR design equations will be solved numerically, specify the information that must be provided and show how to calculate any unknown values.

Numerical Solution of the PFR Design Equations

- Identify the specific set of equations that needs to be solved and within those equations identify the independent and dependent variables, if appropriate, and the unknown quantities to be found by solving the equations.
  - 4 ODEs
  - Independent variable: V
  - Dependent variables: $\dot{n}_A$, $\dot{n}_W$, $\dot{n}_P$ and T
  - Solve for $\dot{n}_A$, $\dot{n}_W$, $\dot{n}_P$ and T at the reactor outlet

$$\frac{d\dot{n}_A}{dV} = f_1\left(V,\dot{n}_A,\dot{n}_W,\dot{n}_P,T\right) = -r$$

$$\frac{d\dot{n}_W}{dV} = f_2\left(V,\dot{n}_A,\dot{n}_W,\dot{n}_P,T\right) = -r$$

$$\frac{d\dot{n}_P}{dV} = f_3\left(V,\dot{n}_A,\dot{n}_W,\dot{n}_P,T\right) = r$$

$$\frac{dT}{dV} = f_4\left(V,\dot{n}_A,\dot{n}_W,\dot{n}_P,T\right)$$

$$= \frac{-r\Delta H^0\left(T\right)}{\dot{n}_A\hat{C}_{p,A} + \dot{n}_W\hat{C}_{p,W} + \dot{n}_P\hat{C}_{p,P}}$$

- Assuming that the PFR design equations will be solved numerically, specify the information that must be provided and show how to calculate any unknown values.

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$$\frac{d\dot{n}_A}{dV} = f_1\left(V,\dot{n}_A,\dot{n}_W,\dot{n}_P,T\right) = -r$$

$$\frac{d\dot{n}_W}{dV} = f_2\left(V,\dot{n}_A,\dot{n}_W,\dot{n}_P,T\right) = -r$$

$$\frac{d\dot{n}_P}{dV} = f_3\left(V,\dot{n}_A,\dot{n}_W,\dot{n}_P,T\right) = r$$

$$\frac{dT}{dV} = f_4\left(V,\dot{n}_A,\dot{n}_W,\dot{n}_P,T\right) = \frac{-r\Delta H^0\left(T\right)}{\dot{n}_A\hat{C}_{p,A} + \dot{n}_W\hat{C}_{p,W} + \dot{n}_P\hat{C}_{p,P}}$$

- Assuming that the PFR design equations will be solved numerically, specify the information that must be provided and show how to calculate any unknown values.
    - Must provide
        - initial values of independent and dependent variables
            - At $V = 0$, $\dot{n}_i = \dot{n}_{i,b} = \dot{n}_{i,a}$ ($i = A$, W and P) and $T = T_b$
        - final value of either the independent variable or one of the dependent variables
            - At the reactor outlet the cumulative volume equals the PFR volume, V
        - code that is given values for the independent and dependent variables and uses them to evaluate the four functions f_1 through f_4
            - In order to evaluate the functions, need to evaluate r and $\Delta H^0(T)$; all other quantities are known constants or will be given

- Evaluation of r
  - Rate expression is given: $r_1 = kC_A C_W \left[1 - \frac{C_P}{KC_A C_W}\right]$
    - Evaluate k and K using given T
      - $k = \left(1.2 \times 10^{12}\ \mathrm{m^3\ kmol^{-1}\ s^{-1}}\right)\exp\left\{\frac{-13000K}{T}\right\}$
      - $K = \left(4.2 \times 10^{-15}\ \mathrm{m^3\ kmol^{-1}}\right)\exp\left\{\frac{11300K}{T}\right\}$
    - Evaluate C_A and C_W using the definition of concentration
      - $C_A = \frac{\dot{n}_A}{\dot{V}} \qquad C_W = \frac{\dot{n}_W}{\dot{V}}$
- Evaluation of $\Delta H^0(T)$
  - $$\Delta H^0(T) = \Delta H^0(298\ \mathrm{K}) + \int_{298K}^{T} \hat{C}_{pP}\, dT - \int_{298K}^{T} \hat{C}_{pA}\, dT - \int_{298K}^{T} \hat{C}_{pW}\, dT$$
    $$= \Delta H^0(298\ \mathrm{K}) + \left(\hat{C}_{pP} - \hat{C}_{pA} - \hat{C}_{pW}\right)\left(T - 298\ \mathrm{K}\right)$$

Heat Exchanger Design Equations

- Set up the heat exchanger design equations (energy balance and either heat transfer equation or specified approach).

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  - Energy balance: $0 = \sum_{\substack{i=all \\ species}} \dot{n}_{i,c} \int_{T_c}^{T_d} \hat{C}_{p,i}\, dT + \sum_{\substack{i=all \\ species}} \dot{n}_{i,a} \int_{T_a}^{T_b} \hat{C}_{p,i}\, dT$
    - $0 = f_5\left(T_b, T_d\right)$

$$= \left(\dot{n}_{A,c}\hat{C}_{p,A} + \dot{n}_{W,c}\hat{C}_{p,W} + \dot{n}_{P,c}\hat{C}_{p,P}\right)\left(T_d - T_c\right) - \left(\dot{n}_{A,a}\hat{C}_{p,A} + \dot{n}_{W,a}\hat{C}_{p,W} + \dot{n}_{P,a}\hat{C}_{p,P}\right)\left(T_b - T_a\right)$$

  - Cold approach: $0 = f_6\left(T_b, T_d\right) = \Delta T_{cold} - T_d - T_a$

Numerical Solution of the Heat Exchanger Design Equations

- Identify the specific set of equations that needs to be solved and within those equations identify the independent and dependent variables, if appropriate, and the unknown quantities to be found by solving the equations.

- Assuming that the heat exchanger design equations will be solved numerically, specify the information that must be provided and show how to calculate any unknown values.

Numerical Solution of the Heat Exchanger Design Equations

- Identify the specific set of equations that needs to be solved and within those equations identify the independent and dependent variables, if appropriate, and the unknown quantities to be found by solving the equations.
  - Two equations

$$0 = f_5\left(T_b, T_d\right) = \left(\dot{n}_{A,c}\hat{C}_{p,A} + \dot{n}_{W,c}\hat{C}_{p,W} + \dot{n}_{P,c}\hat{C}_{p,P}\right)\left(T_d - T_c\right) - \left(\dot{n}_{A,a}\hat{C}_{p,A} + \dot{n}_{W,a}\hat{C}_{p,W} + \dot{n}_{P,a}\hat{C}_{p,P}\right)\left(T_b - T_a\right)$$

$$0 = f_6\left(T_b, T_d\right) = \Delta T_{cold} - T_d - T_a$$

  - Two unknowns: T_b and T_d

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$$0 = f_6\left(T_b,T_d\right) = \Delta T_{cold} - T_d - T_a$$

  - Two unknowns: T_b and T_d

- Assuming that the heat exchanger design equations will be solved numerically, specify the information that must be provided and show how to calculate any unknown values.
  - Must provide guesses for unknowns
  - Code that is given values for the unknowns and uses them to evaluate f_5 and f_6
    - In order to evaluate the functions, need to calculate $\dot{n}_{A,c}$, $\dot{n}_{W,c}$, $\dot{n}_{P,c}$ and T_c; all other quantities are either known constants or will be given
    - Since Tb will be given, the PFR design equations can be solved to find $\dot{n}_{A,c}$, $\dot{n}_{W,c}$, $\dot{n}_{P,c}$ and T_c which can then be used to evaluate f_5 and f_6

Solution

- Solve the design equations and use the results to answer the questions asked.

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- Solve the design equations and use the results to answer the questions asked.
  - Solve the heat exchanger design equations as just described to get T_b and T_d
  - Use the resulting value of T_b to solve the PFR design equations as previously described to get $\dot{n}_{A,c}$, $\dot{n}_{W,c}$, $\dot{n}_{P,c}$ and T_c
  - Calculate the conversion for the integrated heat exchanger and PFR
    - $f_A = \dfrac{\dot{n}_{A,a} - \dot{n}_{A,c}}{\dot{n}_{A,a}}$
  - For the isolated PFR, solve the PFR design equations using the feed temperature (T_a) as previously described to get $\dot{n}_A$, $\dot{n}_W$, $\dot{n}_P$ and T at the reactor outlet
  - Calculate the conversion for the isolated PFR
    - $f_A = \dfrac{\dot{n}_{A,in} - \dot{n}_{A,out}}{\dot{n}_{A,in}}$

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