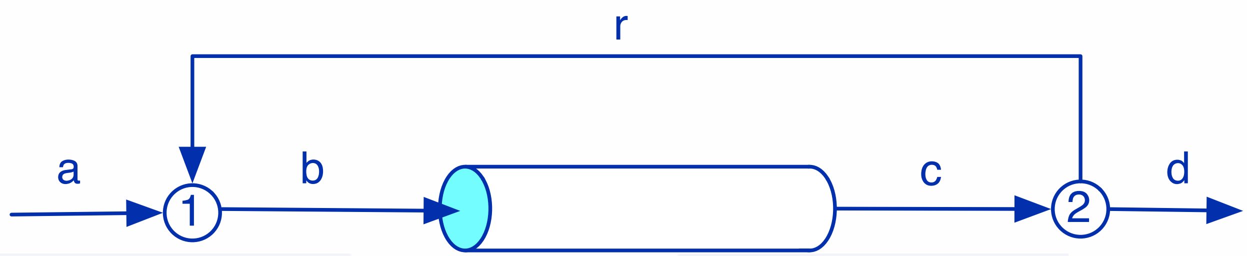
A First Course on Kinetics and Reaction Engineering

Class 33 on Unit 31

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

A Recycle PFR



- The recycle stream, r, mixes a fraction of the product stream with the fresh feed
- The PFR design equations are formulated exactly the same as a stand-alone PFR, but often they cannot be solved independently
  - In those cases, solve them simultaneous with mole and energy balances on the mixing point, 1
  - Define the recycle ratio as the recycle flow, r, divided by the process outlet flow, d
    - $R_R = \frac{\dot{V}_r}{\dot{V}_d} = \frac{\dot{n}_{total,r}}{\dot{n}_{total,d}} = \frac{\dot{n}_{i,r}}{\dot{n}_{i,d}}$
      - As the recycle ratio increases from zero, the reactor becomes less like a PFR and more like a CSTR
  - Mixing point balances: $\dot{n}_{i,a} + \frac{R_R \dot{n}_{i,c}}{1+R_R} - \dot{n}_{i,b} = 0$ $\quad \sum_{\substack{i=all \\ species}} \dot{n}_{i,a} \int_{T_a}^{T_b} \hat{C}_{p,i}\, dT + \sum_{\substack{i=all \\ species}} \dot{n}_{i,r} \int_{T_c(=T_r)}^{T_b} \hat{C}_{p,i}\, dT = 0$
- Caveats
  - Conversion can be defined overall (a to d) or per pass (b to c)
  - Concentrations in the PFR are molar flow rates divided by volumetric flow rate *in the reactor*
    - The flow rate in the reactor is greater than the process feed flow rate
  - Back-mixing introduces the possibility of multiple steady states

Analysis of a Recycle 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 mixing point design equations
  - If the PFR design equations cannot be solved independently
    - Set up the design equations for the mixing point
    - In preparation for solving the mixing point design equations numerically, choose unknowns to be molar flows and temperature of stream b and *do not* choose them as stream c
    - Solve the mixing point design equations numerically
      - The code you must provide will be given the molar flows and temperature of stream b
      - knowing those you can solve the PFR design equations to obtain the molar flows and temperature of stream c
        - knowing those, you can evaluate the mixing point design equations
    - Once the mixing point design equations are solved, use the results to solve the PFR design equations
- Answer the questions posed in the problem statement

Questions?

In liquid phase reaction (1) the chiral molecule, B, is produced autocatalytically according to the rate expression given in equation (2). The heat of reaction is -14 kcal mol^{-1}, independent of temperature. The pre-exponential factor is equal to 4.2 x 10^{15} cm^3 mol^{-1} min^{-1} and the activation energy is 18 kcal mol^{-1}. A solvent is used, and the heat capacity of the reacting solution can be taken to equal that of the solvent, 1.3 cal cm^{-3} K^{-1}. The density of the liquid may be assumed to be constant. The concentrations of A and B in the feed to the process are 2 M and 0 M, respectively, and the flow rate is 500 cm^3 min^{-1} at 300K. An adiabatic recycle PFR with a recycle ratio of 1.3 is used. The reactor diameter is 5 cm and it is 50 cm long. What are the outlet concentrations of A and B and the outlet temperature from the process?

$$A + B \rightarrow 2\,B \qquad (1)$$

$$r_1 = k_1 C_A C_B \qquad (2)$$

Activity 31.1

- In this activity you will practice the general approach for analyzing a recycle PFR
- Perform all work for this activity on the worksheet that has been provided
- Make a sketch of the system, labeling each flow stream

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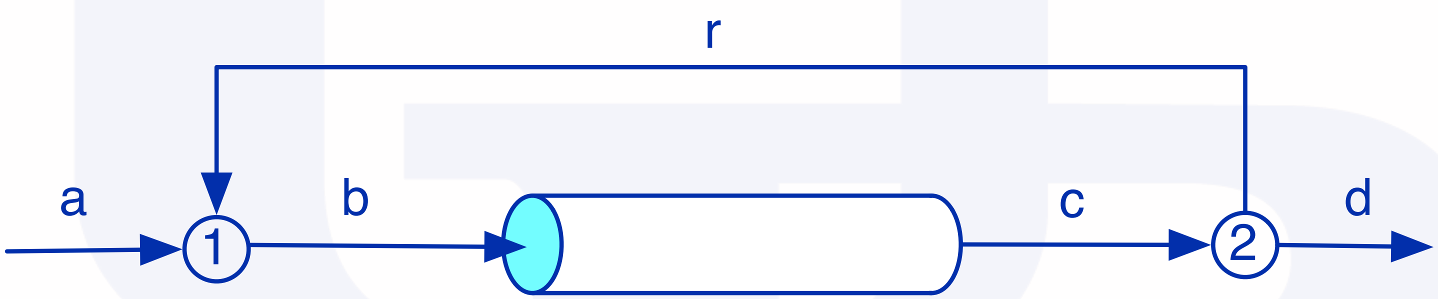

Identify Known Quantities

- 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.

Identify Known Quantities

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  - $\Delta H(T)$ = -14 kcal mol^{-1}
  - k_0 = 4.2 x 10^{15} cm^3 mol^{-1} min^{-1}
  - E = 18 kcal mol^{-1}
  - $\tilde{C}_p$ = 1.3 cal cm^{-3} K^{-1}
  - $C_{A,a}$ = 2 M
  - $C_{B,a}$ = 0 M
  - $\dot{V}_a$ = 500 cm^3 min^{-1}
  - T_a = 300 K
  - R_R = 1.3
  - L = 5 cm
  - D = 50 cm
  - $\dot{V}_d = \dot{V}_a$
  - $\dot{V}_r = R_R \dot{V}_d$
  - $\dot{V}_c = \dot{V}_a + \dot{V}_r$
  - $\dot{V}_b = \dot{V}_c$
  - $\dot{n}_{i,a} = \dot{V}_a C_{i,a}$

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

$$\frac{d\dot{n}_A}{dz} = f_1\left(z,\dot{n}_A,\dot{n}_B,T\right) = -\frac{\pi D^2}{4} r$$

$$\frac{d\dot{n}_B}{dz} = f_2\left(z,\dot{n}_A,\dot{n}_B,T\right) = \frac{\pi D^2}{4} r$$

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

$$\frac{dT}{dz} = f_3\left(z,\dot{n}_A,\dot{n}_B,T\right) = \frac{-\pi D^2}{4}\frac{r\Delta H^0\left(T\right)}{\dot{V}_{in}\tilde{C}_p}$$

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.
  - 3 ODEs
  - Independent variable: z
  - Dependent variables: $\dot{n}_A$, $\dot{n}_B$ and T
  - Solve for $\dot{n}_A$, $\dot{n}_B$ and T at the reactor outlet

$$\frac{d\dot{n}_A}{dz} = f_1\left(z,\dot{n}_A,\dot{n}_B,T\right) = -\frac{\pi D^2}{4}r$$

$$\frac{d\dot{n}_B}{dz} = f_2\left(z,\dot{n}_A,\dot{n}_B,T\right) = \frac{\pi D^2}{4}r$$

$$\frac{dT}{dz} = f_3\left(z,\dot{n}_A,\dot{n}_B,T\right) = \frac{-\pi D^2}{4}\frac{r\Delta H^0\left(T\right)}{\dot{V}_{in}\tilde{C}_p}$$

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$$\frac{d\dot{n}_A}{dz} = f_1\left(z,\dot{n}_A,\dot{n}_B,T\right) = -\frac{\pi D^2}{4} r$$

$$\frac{d\dot{n}_B}{dz} = f_2\left(z,\dot{n}_A,\dot{n}_B,T\right) = \frac{\pi D^2}{4} r$$

$$\frac{dT}{dz} = f_3\left(z,\dot{n}_A,\dot{n}_B,T\right) = \frac{-\pi D^2}{4}\frac{r\Delta H^0\left(T\right)}{\dot{V}_{in}\tilde{C}_p}$$

- 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 $z = 0$, $\dot{n}_i = \dot{n}_{i,b} = \dot{n}_{i,a}$ ($i = A$ and B) and $T = T_b$
    - final value of either the independent variable or one of the dependent variables
      - At the reactor outlet $z = L$
    - code that is given values for the independent and dependent variables and uses them to evaluate the four functions f_1 through f_3
      - In order to evaluate the functions, need to evaluate r; all other quantities are known constants ($\dot{V}_{in} = \dot{V}_b$) or will be given
      - $r = k_1 C_A C_B,\ C_A = \frac{\dot{n}_A}{\dot{V}_b},\ C_B = \frac{\dot{n}_B}{\dot{V}_b},\ k = k_0 \exp\left(\frac{-E}{RT}\right)$

Mixing Point Balance Equations

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$$\dot{n}_{i,a} + \frac{R_R \dot{n}_{i,c}}{1+R_R} - \dot{n}_{i,b} = 0$$

$$\dot{n}_{A,a} + \frac{R_R \dot{n}_{A,c}}{1+R_R} - \dot{n}_{A,b} = f_4\left(\dot{n}_{A,b}, \dot{n}_{B,b}, T_b\right) = 0$$

$$\dot{n}_{B,a} + \frac{R_R \dot{n}_{B,c}}{1+R_R} - \dot{n}_{B,b} = f_5\left(\dot{n}_{A,b}, \dot{n}_{B,b}, T_b\right) = 0$$

$$\sum_{\substack{i=all \\ species}} \dot{n}_{i,a} \int_{T_a}^{T_b} \hat{C}_{p,i}\, dT + \sum_{\substack{i=all \\ species}} \dot{n}_{i,r} \int_{T_c(=T_r)}^{T_b} \hat{C}_{p,i}\, dT = 0$$

$$\dot{V}_a\left(T_b - T_a\right) + \dot{V}_r\left(T_b - T_r\right) = f_6\left(\dot{n}_{A,b}, \dot{n}_{B,b}, T_b\right) = 0$$

Numerical Solution of the Mixing Point 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 mixing point 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 Mixing Point 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.
  - Three equations

$$\dot{n}_{A,a} + \frac{R_R \dot{n}_{A,c}}{1+R_R} - \dot{n}_{A,b} = f_4\left(\dot{n}_{A,b},\dot{n}_{B,b},T_b\right) = 0$$

$$\dot{n}_{B,a} + \frac{R_R \dot{n}_{B,c}}{1+R_R} - \dot{n}_{B,b} = f_5\left(\dot{n}_{A,b},\dot{n}_{B,b},T_b\right) = 0$$

$$\dot{V}_a\left(T_b - T_a\right) + \dot{V}_r\left(T_b - T_r\right) = f_6\left(\dot{n}_{A,b},\dot{n}_{B,b},T_b\right) = 0$$

  - Three unknowns: $\dot{n}_{A,b}$, $\dot{n}_{B,b}$ and T_b
- Assuming that the mixing point 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 Mixing Point Design Equations

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$$\dot{V}_a\left(T_b - T_a\right) + \dot{V}_r\left(T_b - T_r\right) = f_6\left(\dot{n}_{A,b}, \dot{n}_{B,b}, T_b\right) = 0$$

  - Three unknowns: $\dot{n}_{A,b}$, $\dot{n}_{B,b}$ and T_b
- Assuming that the mixing point 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 the unknowns
  - Must provide code that will be given values of the unknowns and must use them to evaluate the functions f_4 through f_6
    - Use the given values of $\dot{n}_{A,b}$, $\dot{n}_{B,b}$ and T_b to solve the PFR design equations for $\dot{n}_{A,c}$, $\dot{n}_{B,c}$ and T_c (= T_r) at which point functions f_4 through f_6 can be evaluated

Solution

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

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  - Solving the mixing point design equations as just described, one finds $\dot{n}_{A,b}$ = 1.07 mol min^{-1}, $\dot{n}_{B,b}$ = 1.23 mol min^{-1} and T_b = 311.5 K
  - Use those values to solve the PFR design equations as previously described, one finds $\dot{n}_{A,c}$ = 0.13 mol min^{-1}, $\dot{n}_{B,c}$ = 2.17 mol min^{-1} and T_c = 320 K = T_d = T_r
  - Knowing the recycle ratio, the molar flow rates in stream d can be found: $\dot{n}_{i,d} = \frac{\dot{n}_{i,c}}{1+R_R}$
    - $\dot{n}_{A,d}$ = 0.056 mol min^{-1} and $\dot{n}_{B,d}$ = 0.94 mol min^{-1}
  - The corresponding concentrations can then be found: $C_{i,d} = \frac{\dot{n}_{i,d}}{\dot{V}_d}$
    - $C_{A,d}$ = 0.11 M and $C_{B,d}$ = 1.89 M

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