

The background features a large, stylized blue and grey buffalo mascot. The buffalo is facing forward with its mouth open, showing its teeth. Below the buffalo's head, the word "BUFFALO" is written in a large, bold, white, italicized font with a grey outline. The text is centered horizontally and spans most of the width of the page.

A First Course on Kinetics and Reaction Engineering

Class 34 on Unit 32

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**



Semi-Batch (Semi-Flow) Reactor

- A batch reactor where some reactant flows in or some product flows out while the batch is processing
 - ▶ Neutralization of an acid with a base
 - Add base slowly to batch of acid in order to control the rate at which heat is released
 - ▶ Reversible esterification
 - Allow one product to boil off allowing the reaction to reach higher conversion than in a closed batch process
- If species are boiling off, the composition of the leaving vapor is related to the composition of the liquid, e. g. by Raoult's law or Henry's law
- Unlike common batch reactors, often the fluid volume is not constant
 - ▶ Use the appropriate equation of state to re-write the derivatives of fluid volume and pressure in terms of the moles in the reactor and the temperature



Semi-Batch Design Equations

- Mole balance

- ▶ \dot{n}_i is the net molar rate of flow of species i into the reactor

- may be a function of time

$$\frac{dn_i}{dt} = \dot{n}_i + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j$$

- Energy balance

- ▶ $\sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_i (\hat{h}_i - \hat{h}_{i,\text{stream}})$ is the energy used in heating the incoming stream to the reactor temperature and doing the P-V work associated with flowing in

- ▶ Usually,

$$\dot{n}_i (\hat{h}_i - \hat{h}_{i,\text{stream}}) = \dot{n}_i \left(\int_{T_{\text{stream}}}^T \hat{C}_{p,i} dT + \Delta H_{\text{latent},i} \right)$$

$$\begin{aligned} \dot{Q} - \dot{W} = & \sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_i (\hat{h}_i - \hat{h}_{i,\text{stream}}) + \frac{dT}{dt} \sum_{\substack{i=\text{all} \\ \text{species}}} (n_i \hat{C}_{pi}) \\ & + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} (r_j \Delta H_j) - \frac{dP}{dt} V - P \frac{dV}{dt} \end{aligned}$$



Questions?



The reaction between A and B produces the desired product, D according to reaction (1), but B also decomposes according to reaction (2), generating the undesired product U. The reactions take place in solution, and the heat of reaction is so small that the reactions are effectively isothermal. Reaction (1) is first order in each of the two reactants, second order overall. Reaction (2) is second order in B. At the process temperature the rate coefficient for reaction (1) is $8 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$ and that for reaction (2) is $4 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$. A 2000 L stirred tank reactor will be used, taking its feed from one solution containing A at a concentration of 3 mol L^{-1} and from a second containing B at a concentration of 1 mol L^{-1} . Compare the selectivity (mol D per mol U) that will result from a batch process charged with 500 L of the A solution and 1500 L of the B solution to a semi-batch process where the reactor is charged with 500 L of the A solution at which time the B solution flows into the reactor at a rate of 150 L h^{-1} . In both cases, allow the reaction to proceed to a 95% conversion of B; in the semi-batch system, this may require stopping the flow when the reactor contains 2000 L of solution and allowing it to continue to react as a batch reactor until the desired conversion is reached.



Activity 32.1

- In class, we will not perform the batch reactor analysis
 - ▶ Doing so, one finds
 - 651 minutes are required to reach 95% conversion of B in a batch reactor
 - At the end of the batch process there are 3.2 moles of D per mole of U
- Here, we will begin with the analysis of semi-batch operation
- Before beginning the analysis of semi-batch operation, mentally perform a qualitative analysis and predict whether (a) the semi-batch processing will take more or less time than batch processing and (b) whether the final selectivity in semi-batch processing will be larger or smaller than that in batch processing



Activity 32.1

- In class, we will not perform the batch reactor analysis
 - ▶ Doing so, one finds
 - 651 minutes are required to reach 95% conversion of B in a batch reactor
 - At the end of the batch process there are 3.2 moles of D per mole of U
- Here, we will begin with the analysis of semi-batch operation
- Before beginning the analysis of semi-batch operation, mentally perform a qualitative analysis and predict whether (a) the semi-batch processing will take more or less time than batch processing and (b) whether the final selectivity in semi-batch processing will be larger or smaller than that in batch processing
 - ▶ By adding a reactant slowly over time, the concentration of that reactant will be low at all times.
 - This will cause the rate to be low and therefore it will take longer to reach a given conversion than a batch reactor would
 - Keeping the concentration of B low at all times will have a greater effect on the undesired reaction (second order in B) than the desired reaction (first order in B), so the selectivity will be greater than a batch reactor



- Read through the problem statement, and each time you encounter a quantity, write it down and equate it to the appropriate variable
 - ▶ If there are any additional constant quantities that you know will be needed and that can be calculated from the values given in the problem statement, write the equations needed for doing so



- Read through the problem statement, and each time you encounter a quantity, write it down and equate it to the appropriate variable
 - ▶ $k_1 = 8 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$, $k_2 = 4 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$, $V_{max} = 2000 \text{ L}$, $C_{A,0} = 3 \text{ mol L}^{-1}$,
 $C_{B,0} = 1 \text{ mol L}^{-1}$, $V_{A,0} = 500 \text{ L}$, $\dot{V}_B = 150 \text{ L h}^{-1}$, $f_B = 0.95$
- If there are any additional constant quantities that you know will be needed and that can be calculated from the values given in the problem statement, write the equations needed for doing so



- Read through the problem statement, and each time you encounter a quantity, write it down and equate it to the appropriate variable
 - ▶ $k_1 = 8 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$, $k_2 = 4 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$, $V_{max} = 2000 \text{ L}$, $C_{A,0} = 3 \text{ mol L}^{-1}$, $C_{B,0} = 1 \text{ mol L}^{-1}$, $V_{A,0} = 500 \text{ L}$, $\dot{V}_B = 150 \text{ L h}^{-1}$, $f_B = 0.95$
- If there are any additional constant quantities that you know will be needed and that can be calculated from the values given in the problem statement, write the equations needed for doing so
 - ▶ $n_{A,0} = V_0 C_{A,0}$
 - ▶ $\dot{n}_B = \dot{V}_B C_{B,0}$
- Generate the design equations needed to model the semi-batch reactor by simplification of the general design equations found in Unit 32 or on the AFCoKaRE Exam Handout



- General form of the mole balance design equation: $\frac{dn_i}{dt} = \dot{n}_i + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j$

- ▶ Here, 2 reactions so summation expands to 2 terms

- ▶ Only B flows in or out of the reactor, so $\dot{n}_A = \dot{n}_D = \dot{n}_U = 0$

- ▶ $\frac{dn_A}{dt} = -Vr_1$

- ▶ $\frac{dn_B}{dt} = \dot{n}_B + V(-r_1 - 2r_2)$

- ▶ $\frac{dn_D}{dt} = Vr_1$

- ▶ $\frac{dn_U}{dt} = Vr_2$

- Determine whether the design equations can be solved once, covering the entire semi-batch process, or whether they will need to be solved in stages
 - ▶ If they need to be solved in stages, identify the beginning and end of each stage



- General form of the mole balance design equation: $\frac{dn_i}{dt} = \dot{n}_i + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j$

- ▶ Here, 2 reactions so summation expands to 2 terms

- ▶ Only B flows in or out of the reactor, so $\dot{n}_A = \dot{n}_D = \dot{n}_U = 0$

- ▶ $\frac{dn_A}{dt} = -Vr_1$

- ▶ $\frac{dn_B}{dt} = \dot{n}_B + V(-r_1 - 2r_2)$

- ▶ $\frac{dn_D}{dt} = Vr_1$

- ▶ $\frac{dn_U}{dt} = Vr_2$

- Determine whether the design equations can be solved once, covering the entire semi-batch process, or whether they will need to be solved in stages

- ▶ If they need to be solved in stages, identify the beginning and end of each stage

- Stage 1 (semi-batch): starts when flow of B into the reactor starts; ends when flow of B into the reactor ends

- Stage 2 (batch): starts immediately after stage 1 ends, ends when the conversion of B reaches 95%



- General form of the mole balance design equation: $\frac{dn_i}{dt} = \dot{n}_i + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} v_{i,j} r_j$

- ▶ Here, 2 reactions so summation expands to 2 terms

- ▶ Only B flows in or out of the reactor, so $\dot{n}_A = \dot{n}_D = \dot{n}_U = 0$

- ▶ $\frac{dn_A}{dt} = -Vr_1$

- ▶ $\frac{dn_B}{dt} = \dot{n}_B + V(-r_1 - 2r_2)$

- ▶ $\frac{dn_D}{dt} = Vr_1$

- ▶ $\frac{dn_U}{dt} = Vr_2$

- Determine whether the design equations can be solved once, covering the entire semi-batch process, or whether they will need to be solved in stages

- ▶ If they need to be solved in stages, identify the beginning and end of each stage

- Stage 1 (semi-batch): starts when flow of B into the reactor starts; ends when flow of B into the reactor ends

- Stage 2 (batch): starts immediately after stage 1 ends, ends when the conversion of B reaches 95%

- ▶ If \dot{n}_B is set equal to zero in stage 2, the same equations can be used for both stages



- For each stage of the solution, 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



- For each stage of the solution, 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

- ▶ $\frac{dn_A}{dt} = f_1(t, n_A, n_B, n_D, n_U) = -Vr_1$

- ▶ $\frac{dn_B}{dt} = f_2(t, n_A, n_B, n_D, n_U) = \dot{n}_B + V(-r_1 - 2r_2)$

- ▶ $\frac{dn_D}{dt} = f_3(t, n_A, n_B, n_D, n_U) = Vr_1$

- ▶ $\frac{dn_U}{dt} = f_4(t, n_A, n_B, n_D, n_U) = Vr_2$

- ▶ Solving the equations will yield the values of t , n_A , n_B , n_D and n_U at the end of the stage
- Assuming that the semi-batch reactor design equations will be solved numerically, specify the information that must be provided and show how to calculate any unknown values for each stage of the solution



- For each stage of the solution, 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

- ▶ $\frac{dn_A}{dt} = f_1(t, n_A, n_B, n_D, n_U) = -Vr_1$

- ▶ $\frac{dn_B}{dt} = f_2(t, n_A, n_B, n_D, n_U) = \dot{n}_B + V(-r_1 - 2r_2)$

- ▶ $\frac{dn_D}{dt} = f_3(t, n_A, n_B, n_D, n_U) = Vr_1$

- ▶ $\frac{dn_U}{dt} = f_4(t, n_A, n_B, n_D, n_U) = Vr_2$

- Assuming that the semi-batch reactor design equations will be solved numerically, specify the information that must be provided and show how to calculate any unknown values for each stage of the solution
 - ▶ Initial conditions
 - values of independent and dependent variables at start of each stage
 - ▶ Final conditions
 - stage 1: time that addition of B ends
 - stage 2: moles of B present when conversion reaches 95%
 - ▶ Code to evaluate f_1 through f_4 given independent and dependent variables



- Stage 1

- ▶ Initial conditions

- $t = 0, n_A = n_{A,0}, n_B = n_D = n_U = 0$

- ▶ Final condition

- Flow of B stops when $V = V_{max}$

$$V = V_0 + \dot{V}_B t$$

$$V_{max} = V_0 + \dot{V}_B t_{f,1} \Rightarrow t_{f,1} = \frac{V_{max} - V_0}{\dot{V}_B}$$

- ▶ Code to evaluate f_1 through f_4

- Need to first calculate r_1 and r_2

$$r_1 = k_1 C_A C_B$$

$$r_2 = k_2 C_B^2$$

- Need to calculate C_A and C_B

$$C_A = \frac{n_A}{V} \quad C_B = \frac{n_B}{V} \quad V = V_0 + \dot{V}_B t$$

- Stage 2

- ▶ Initial conditions

- equal to final values of t, n_A, n_B, n_D and n_U from stage 1

- ▶ Final condition

$$n_B = \dot{n}_B t_{f,1} (1 - f_B)$$

- ▶ Code as above

- Identify what variables will become known upon solving the design equations and show how those variables can be used to answer the questions that were asked in the problem



- Solving the design equations gives the time for each of the two stages and the final moles of A, B, D and U for each of the two stages

- ▶ $t_{semi} = t_{f,1} + t_{f,2}$

- ▶ $S_{D/U} = \frac{n_{D,f,2}}{n_{U,f,2}}$



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
- **Part IV - Non-Ideal Reactions and Reactors**
 - ▶ A. Alternatives to the Ideal Reactor Models
 - 33. Axial Dispersion Model
 - 34. 2-D and 3-D Tubular Reactor Models
 - 35. Zoned Reactor Models
 - 36. Segregated Flow Model
 - 37. Overview of Multi-Phase Reactors
 - ▶ B. Coupled Chemical and Physical Kinetics

