A First Course on Kinetics and Reaction Engineering

Class 12 on Unit 12

Where We're Going

- Part I - Chemical Reactions
- **Part II - Chemical Reaction Kinetics**
  - ▸ A. Rate Expressions
  - ▸ B. Kinetics Experiments
    - 11. Laboratory Reactors
    - 12. Performing Kinetics Experiments
  - ▸ C. Analysis of Kinetics Data
- **Part III - Chemical Reaction Engineering**
- **Part IV - Non-Ideal Reactions and Reactors**

Testing Reactor Models

- If mixing is perfect, the rate of reaction should not depend upon agitator speed
- Interfacial Gradients
  - The ideal reactor models assume locally uniform composition
  - When two phases coexist, concentration and/or temperature gradients develop near the interface between the phases
    - Gradients between the bulk fluid and the surface can cause external transport limitations
    - Gradients within the pores of a solid can cause internal transport limitations
  - Experimental and computational tests can be performed to make sure the rate is negligibly affected by these gradients
- External transport limitation tests
  - The conversion should not vary with linear flow velocity if the residence time is constant
    - At very low flow rates this test lacks sensitivity
  - Be suspicious of first order kinetics with very low activation energies
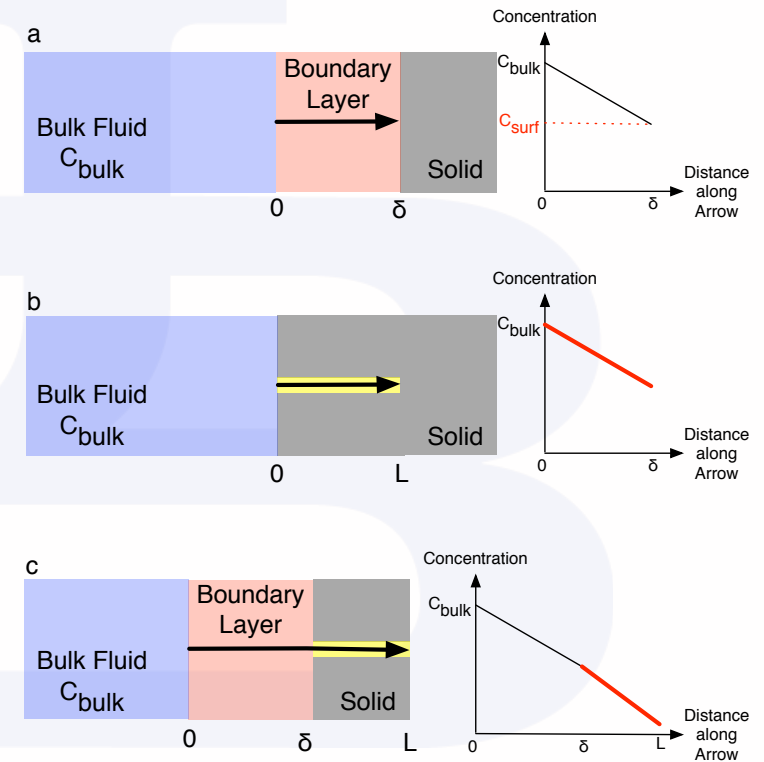
Testing for Transport Limitations and Performing Kinetics Experiments

- Computational tests for external transport limitations

$$\frac{(-\Delta H)(-r)r_p}{hT} < 0.15\frac{RT}{E} \qquad \frac{(-r)r_p}{Ck_c} < \frac{0.15}{n} \qquad \frac{|\Delta H|(-r)r_r^2}{\lambda T_w} < 0.4\frac{RT_w}{E}$$

- Experimental test for internal transport limitations
  - For fixed residence time, the conversion should not vary as a function of catalyst particle size
  - For fixed dispersion of supported catalysts, the conversion should not vary with catalyst loading
  - Be suspicious if the activation energy drops by 50% at higher temperatures

- Computational tests for internal transport limitations

$$\phi_s = \frac{r_p^2(-r)}{D_{eff}C} \qquad \frac{r_p^2(-r)\Delta H}{\lambda T} < 0.75\frac{RT}{E}$$

- Typical kinetics experiments
  - Batch reactor: charge and bring to temperature, measure initial composition
    - measure composition vs. time
    - several data points per experiment
  - Flow reactors: set inlet conditions and temperature, wait until system is at steady state
    - measure outlet composition
    - one data point per experiment

Kinetics Experiments

- Three possible objectives
  - ▸ Determine whether the reaction is reversible by attempting to attain 100% conversion of the limiting reagent
  - ▸ Conduct a few experiments where "base conditions" are selected and concentration of each reagent is changed holding all others constant
    - - Results can help when guessing a rate expression to test
  - ▸ Gather data that span all possible temperatures and compositions of interest for the resulting rate expression

- Experimental approach
  - ▸ Operate the reactor in the preferred mode to simplify data analysis
  - ▸ Conduct experiments in constant temperature blocks
    - - Analyze data in two steps: first by block to get rate coefficient(s) at each block temperature
    - - Then analyze rate coefficients vs. block temperatures to get Arrhenius parameters
  - ▸ Consider statistical design of experiments

Questions?

Activity 12.1
Four Slide Presentation

Units 11 and 12 presented a number of different procedures for "testing" laboratory reactors. Prepare a four slide presentation that summarizes the important information. You can simply sketch out your slides on paper; you do not need to actually prepare slides (you may, if you wish).

The recommended format for the presentation is to use the first slide to describe why the tests are necessary and what they actually test. The remaining three slides should be devoted to actual tests, organized in some logical order.

A few of you may be called upon to show your slides and describe the points you would seek to make with each slide.

Key Points

- It's imperative to test that a laboratory reactor can be modeled accurately
- Age function tests use stimulus and compare actual response to ideal reactor response
- Flow visualization and age function tests can prove the model inaccurate, but they can't prove it is accurate
- Perfect mixing can be tested using the agitator speed test
- When 2 or more phases are present there will be interfacial gradients in concentration and temperature
  - They can't be eliminated; it must be demonstrated that they have a negligibly small effect
- For heterogeneous catalysis, transport limitations are separated into internal and external effects
  - For each type there are experimental and computational tests

Activity 12.2

- Example 12.5 indicated that there are differences between the kinetics data generated using a batch reactor and those generated using a CSTR
  - ‣ There are also differences in the experiments used to generate the data
- In this activity, the nature of these differences will be observed using kinetics simulators for a batch reactor and a CSTR
  - ‣ Apart from batch versus continuous, what experimental aspects are different?
  - ‣ How can these differences be rationalized without resorting to equations?
  - ‣ What implications might these differences have upon the data analysis?
- As you work, you should copy your simulator results to the Excel handout 12_Activity_2.xlsx
  - ‣ As you work through the activity, you will enter simulator results in cells that are colored green
  - ‣ As you fill in those results, values will appear in cells colored yellow and blue
- Generation of batch reactor kinetics data using a single experiment
  - ‣ Set $T = 340\ ^{\circ}C$, $V = 5$ L, $C_A = C_B = 1.0$ M and $C_X = C_Y = 0.0$ M
  - ‣ Start the experiment and watch the concentration of Y
    - - Record a data point when C_Y is approximately 0.2, 0.4, 0.6, 0.8 and 0.9 M
    - - Note any trends you observe
  - ‣ Fill in the results in the cells of the batch reactor table (top, left) that are colored light green

- Generate CSTR data using the same feed composition and reaction times
  - The upper CSTR data table on the spreadsheet should be pre-filled in except for the last two columns
    - Each row is a separate CSTR experiment
    - The feed composition for every experiment is the same as the initial composition in the batch experiment; the temperatures are the same, as well
    - The feed flow rates have been filled in for you so that the CSTR residence times are equal to the elapsed times for your five batch reactor experiments
  - Use the CSTR simulator to perform the 5 experiments using the settings in the table
    - Record the outlet temperature and concentration of Y for each experiment in the spreadsheet
  - Note any trends you observe
  - Note any differences you observe between the batch experiment or data and the CSTR
- Generate alternative CSTR data where the CSTR feed composition equals the batch reactor composition at the start of a batch reactor interval and the residence time in the CSTR equals the length of the batch reactor interval
  - The lower CSTR data table on the spreadsheet should again be pre-filled in except for the last two columns
  - Note, in this series of experiments, the CSTR feed simulates the batch reactor composition at the start of each of the five sampling intervals
    - The CSTR feed rate has been calculated so that the CSTR residence time is equal to the elapsed time until the next batch reactor sample was taken
  - As above, use the CSTR simulator to perform the 5 experiments using the settings in the table
  - Note any trends and and differences between the batch experiment or data and the CSTR

Procedure Summary

- Generation of batch reactor kinetics data using a single experiment
  - ‣ Set T = 340 °C, V = 5 L, C_A = C_B = 1.0 M and C_X = C_Y = 0.0 M
  - ‣ Start the experiment and watch the concentration of Y
    - − Record a data point when C_Y is approximately 0.2, 0.4, 0.6, 0.8 and 0.9 M
    - − Note any trends you observe
  - ‣ Fill in the results in the cells of the batch reactor table (top, left) that are colored light green
- Generate CSTR data using the same feed composition and reaction times
  - ‣ Use the CSTR simulator to perform the 5 experiments using the settings in the upper CSTR table
    - − Record the outlet temperature and concentration of Y for each experiment in the spreadsheet
  - ‣ Note any trends you observe
  - ‣ Note any differences you observe between the batch experiment or data and the CSTR
- Generate alternative CSTR data
  - ‣ As above, use the CSTR simulator to perform the 5 experiments using the settings in the lower CSTR table
    - − Record the outlet temperature and concentration of Y for each experiment in the spreadsheet
  - ‣ Note any trends you observe
  - ‣ Note any differences you observe between the batch experiment or data and the CSTR

Discuss and Rationalize

- List trends you observed in the batch experiment and data
  - ‣ Offer a qualitative explanation for the trend; you may not use an equation to explain the trend
- List trends you observed in the CSTR experiment and data
  - ‣ Offer a qualitative explanation for the trend; you may not use an equation to explain the trend
- List the differences you observed between the batch experiment/results and the CSTR experiment/results
  - ‣ Offer a qualitative explanation for the differences
  - ‣ Discuss what implications the differences might have upon the use of the data for the testing of a rate expression
- Can you think of a way to eliminate the differences between the two sets of data?

Discuss and Rationalize

- List trends you observed in the batch experiment and data
  - ‣ The time required for the concentration of Y to increase by 0.2 M gets longer and longer as the reaction proceeds
    - It takes 0.17 min to go from 0.0 to 0.2 M
    - It takes 0.28 min to go from 0.2 to 0.4 M
    - It takes 0.53 min to go from 0.4 to 0.6 M, etc.
  - ‣ This makes sense because one expects the rate to decrease as the reactant concentrations decrease; if the rate is smaller, it will take longer
    - The average reactant concentration is 0.9 M during the time that the product goes from 0.0 to 0.2 M
    - The average reactant concentration is 0.7 M during the time that the product goes from 0.2 to 0.4 M
    - The average reactant concentration is 0.5 M during the time that the product goes from 0.4 to 0.6 M, etc

Discuss and Rationalize

- List trends you observed in the batch experiment and data
  - ‣ The time required for the concentration of Y to increase by 0.2 M gets longer and longer as the reaction proceeds
    - This makes sense because one expects the rate to decrease as the reactant concentrations decrease; if the rate is smaller, it will take longer

- **List trends you observed in the CSTR experiment and data**
  - ‣ Similar to the batch reactor, the space time required for an equal change in the product concentration gets longer as the conversion gets higher
    - The reason is the same; the rate decreases as the reactant concentrations decrease

Discuss and Rationalize

- List trends you observed in the batch experiment and data
  - ▸ The time required for the concentration of Y to increase by 0.2 M gets longer and longer as the reaction proceeds
    - This makes sense because one expects the rate to decrease as the reactant concentrations decrease
- List trends you observed in the CSTR experiment and data
  - ▸ Similar to the batch reactor, the space time required for an equal change in the product concentration gets longer as the conversion gets higher
    - The reason is the same; the rate decreases as the reactant concentrations decrease
- **List the differences you observed between the batch experiment/results and the CSTR experiment/results**
  - ▸ For equal reaction times, the change in the product concentration in the CSTR is smaller than the change in the batch reactor
    - This makes sense because on average, the reactant concentration is smaller in the CSTR, so the rate is smaller
    - Starting with $C_A = C_B = 1.0$ M and $C_X = C_Y = 0.0$ M and reacting for ~0.17 min
      - The reactant concentration in the batch reactor ranges from 1.0 M to 0.8 M for an average of 0.9 M
      - The reactant concentration in the CSTR is equal to 0.82 M the whole time
  - ▸ The differences are smaller when the concentration change in the batch reactor is smaller (i. e. when the CSTR experiments correspond to intervals between successive data points instead of the interval since the first data point)
    - This makes sense because the average batch reactor reactant concentrations are closer the CSTR concentrations

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Discuss and Rationalize

- Discuss what implications the differences might have upon the use of the data for the testing of a rate expression
  - ‣ In a CSTR experiment, the reaction takes place at constant concentration and therefore at constant rate
    - For any one data point, it is easy to relate the concentration to the rate
  - ‣ In a batch reactor experiment, the reaction takes place over a range of concentrations and therefore over a range of rates
    - For any one data point, the concentration change is related to an integral over the range of rates that prevail between the initial and final compositions
  - ‣ Analysis of batch reactor data will require some form of integration; analysis of CSTR data will not

Discuss and Rationalize

- Discuss what implications the differences might have upon the use of the data for the testing of a rate expression
    - In a CSTR experiment, the reaction takes place at constant concentration and therefore at constant rate
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    - Analysis of batch reactor data will require some form of integration; analysis of CSTR data will not

- Can you think of a way to eliminate the differences between the two sets of data?
    - Run the batch reactor for very short periods of time
        - If the concentration only changes slightly, the average concentration during the batch experiment will be approximately equal to both the starting and ending concentration
        - The rate can then be related to the average concentration without significant error, and it isn't necessary to integrate over a range of rates

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    - 11. Laboratory Reactors
    - 12. Performing Kinetics Experiments
  - ▸ C. Analysis of Kinetics Data
    - 13. CSTR Data Analysis
    - 14. Differential Data Analysis
    - 15. Integral Data Analysis
    - 16. Numerical Data Analysis
- **Part III - Chemical Reaction Engineering**
- **Part IV - Non-Ideal Reactions and Reactors**