A First Course on Kinetics and Reaction Engineering

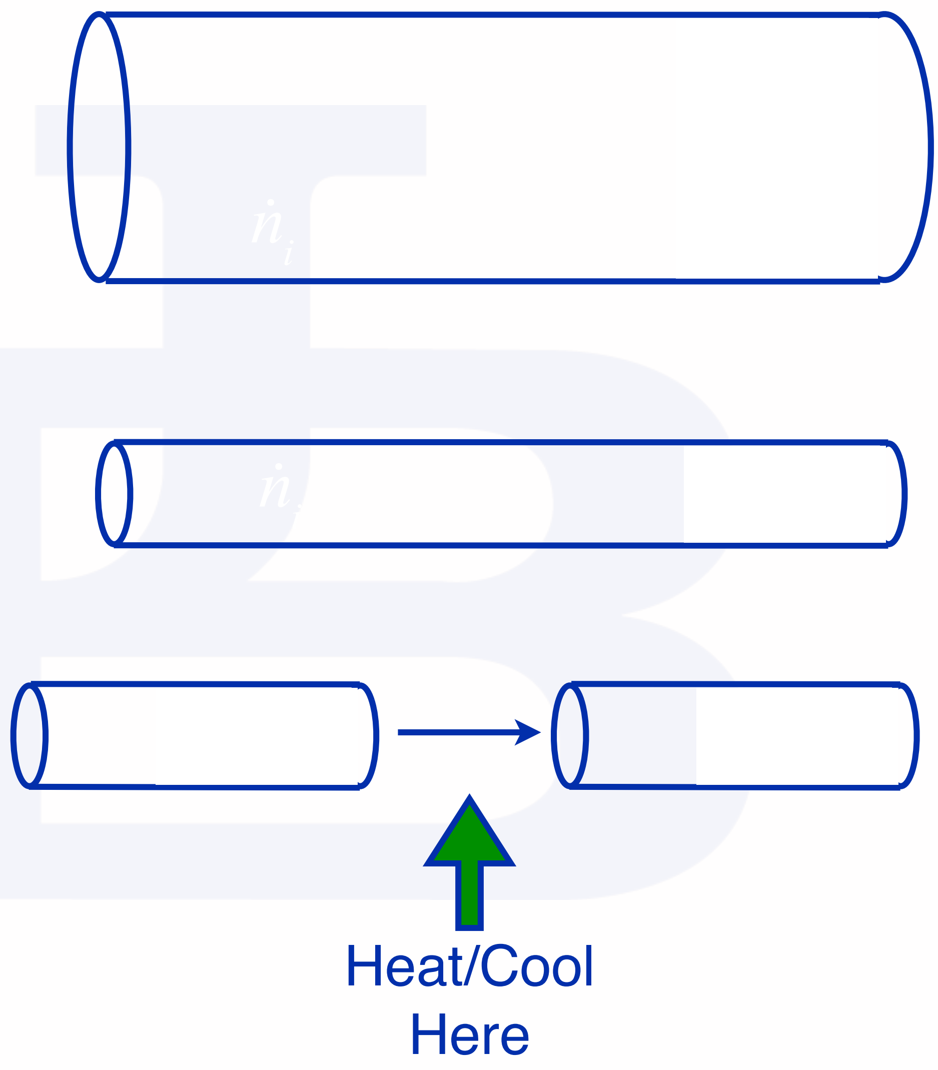
Class 26 on Unit 25

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
        - 25. Reaction Engineering of PFRs
        - 26. Analysis of Steady State PFRs
        - 27. Analysis of Transient PFRs
    - E. Matching Reactors to Reactions
- Part IV - Non-Ideal Reactions and Reactors

PFR Characteristics

- Environmental variables change along length of reactor
- Heat transfer area is limited to the reactor wall
- Area to Volume is more limited than a CSTR
  - Can't add a coil inside the fluid
- Only option for increasing area is to use smaller diameter tube
  - Eventually leads to large pressure drop through reactor
- Sometimes can break reactor into segments with some form of heating/cooling between them

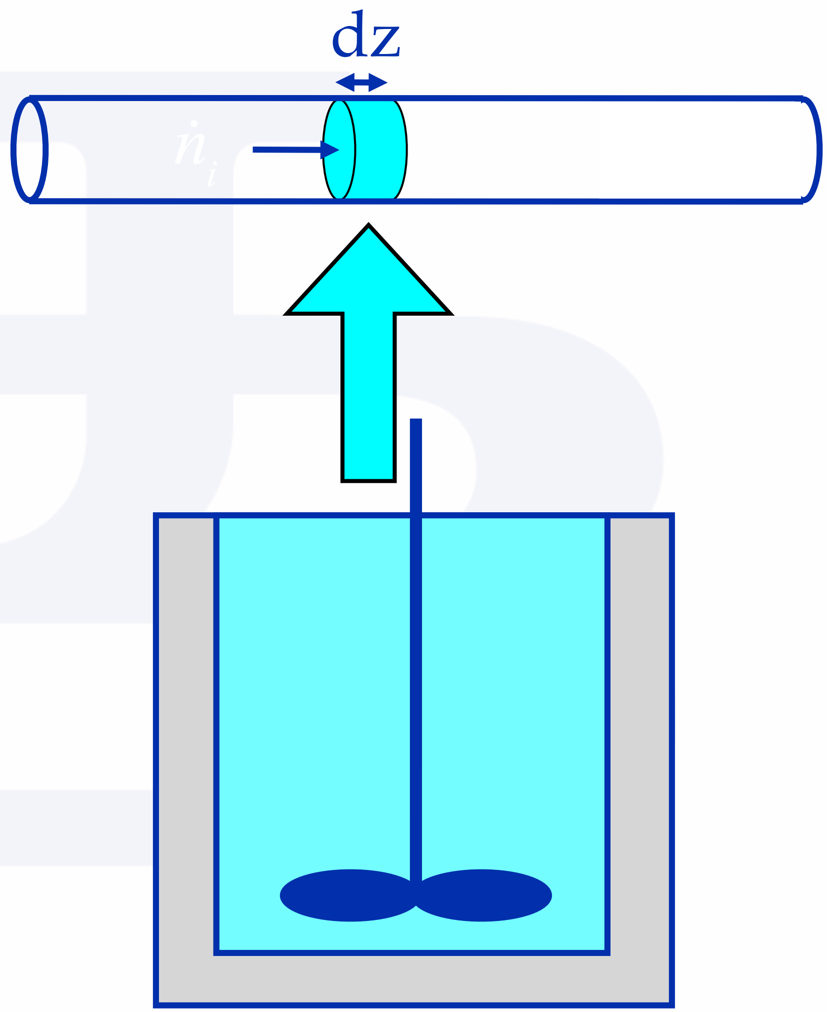


PFR Advantages & Disadvantages

- Distinguishing Features
  - No agitation
    - Equally well-suited to gases and liquids
    - Preferred if a solid catalyst is being used because less abrasion
  - Reactant concentration decreases continually and product concentration increases continually from inlet to outlet
  - Temperature may vary over the length of the reactor
- Preferred Uses
  - Reactions that require a solid catalyst
  - Large quantities of reactant to be processed
  - Reactions that will be run adiabatically or with little heating/ cooling
  - Reactions with "typical" kinetics
    - High rate or selectivity is favored by high reactant concentration and low product concentration
    - Same kinds of reactions as are favored in a batch reactor
  - Reversible reactions

Analogy between
Batch Reactors and PFRs

- Fluid element within a PFR is like a batch reactor
  - perfectly mixed radially
  - differentially thick so negligible axial differences
  - no fluid enters the element or leaves it during process
- Starts reacting when fluid element enters the reactor and stops when it leaves
  - processing time is equal to the residence time (space time)
- Qualitatively, PFR performance as a function of space time is the same as the qualitative performance of a batch reactor as a function of processing time



A General Approach to Solving Qualitative Reaction Engineering Problems

- Read through the problem statement and identify
  - the type of reactor being used
  - the reactor operating procedure (isothermal vs. adiabatic, steady state vs. transient, etc.)
  - the type of reaction(s) taking place (reversible/irreversible, series, etc.) and their kinetics (typical, given rate expression, auto-catalytic, product inhibited, etc.)
  - the quantities whose variation you are asked to describe
- Determine initial trends in reactant concentration(s), product concentrations, temperature, reaction rate and other quantities of interest versus time[1]
  - Draw axes for each plot
  - Determine the value of each quantity time zero and plot it
  - Consider the first small increment in time
    - Based on the rate at the start of this time interval determine the initial slope for every plot except the rate and sketch it on the plot
    - Based on how the concentrations and temperature change during this interval, determine how the rate will change and use the answer to sketch it on the rate plot
    - if comparing two or more systems, for each plot, determine the which system will have the largest slope, the second largest slope, etc.

[1] Here "time" should be taken to mean processing time for a batch reactor and space time for a CSTR or PFR

General Approach (continued)

- Consider the next small increment in time
  - Based on the rate at the start of this interval compared to the rate at the start of the previous interval, determine whether the slope in this interval will be larger, the same or smaller. Use the answer to sketch the initial curvature for every plot except the rate
  - Based on how the concentrations and temperature change during this interval, determine how the rate will change during this interval and compare it to how the rate changed during the previous interval. Use the answer to sketch the initial curvature of the rate plot

- Determine whether continuing the initial trends will result in the rate asymptotically approaching zero and the other quantities asymptotically approaching their equilibrium values.
  - If not, use the given kinetics information to infer what must happen so that the system does approach equilibrium properly and modify the plots accordingly
  - If comparing two or more systems, note that the asymptotic limits may differ if the equilibrium conversion is affected by temperature changes
- Use the final sketched plots to answer the questions posed in the problem

Questions?

Activity 25.1

Suppose reaction (1) and reaction (2) are typical irreversible reactions and further assume that they have exactly the same rate expression (same reaction orders, same pre-exponential factor and same activation energy). In fact, the only difference between them is that reaction (1) is exothermic and reaction (2) is endothermic. Make a single graph showing conversion of A versus space time, and on that graph sketch what the plot would look like (a) for reaction (1) taking place in an adiabatic PFR, (b) for reaction (1) taking place in an isothermal PFR, (c) reaction (2) taking place in an adiabatic PFR and (d) reaction (2) taking place in an isothermal PFR. For each plot explain why it has the shape it does, and then explain why the plots differ from each other in the way they do.

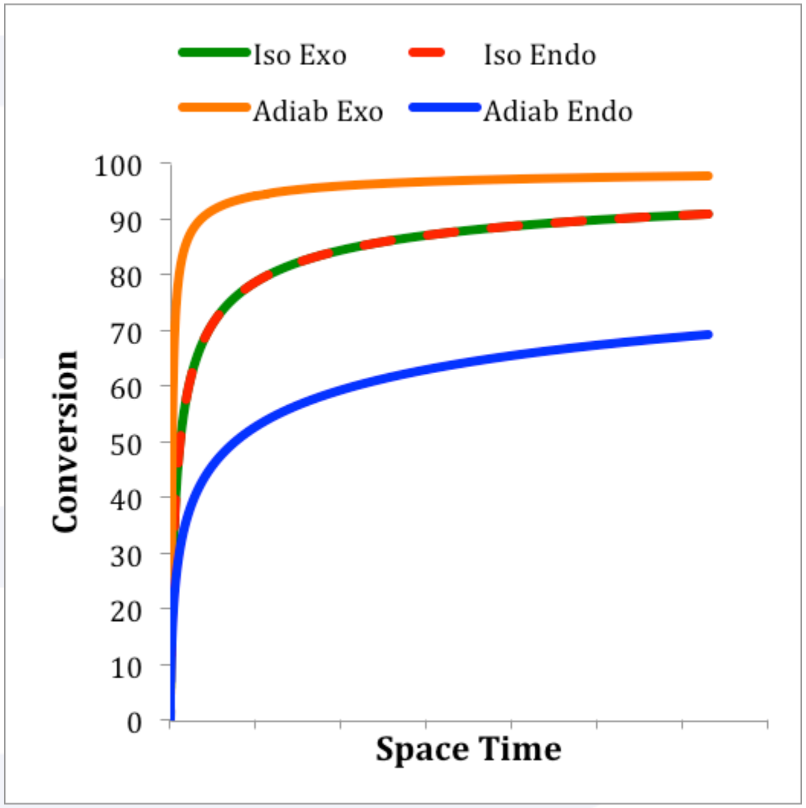
$$A \rightarrow B \qquad (1)$$

$$A \rightarrow C \qquad (2)$$

Key plot features you should incorporate *and justify* are initial values, slopes and curvature, additional inflection points, maxima, etc. (if needed in order to asymptotically approach equilibrium) and relative curve positions, crossings, etc.

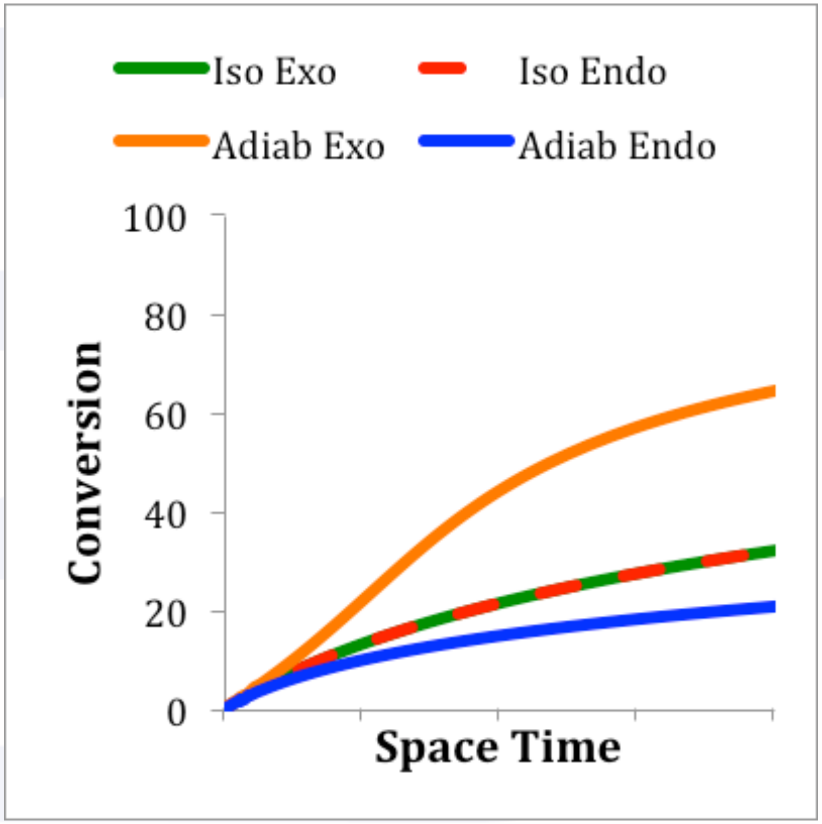
Analysis

- Isothermal systems will be identical because kinetics are the same
  - Start at zero conversion
    - No reaction before entering reactor
  - Positive slope
    - High reactant concentration, high rate, reactant consumed, conversion increases
  - Concave down
    - Farther into the reactor, reactant concentration smaller, rate smaller, not as much conversion
  - Asymptotically approaches 100% conversion
    - At which point slope equals zero
- Adiabatic systems will differ due to temperature effects
  - Endothermic reaction, as conversion increases, temperature decreases, rate decreases beyond decrease seen in isothermal
  - Same shape as isothermal, but always below isothermal curve



Adiabatic Exothermic Analysis

- Competing effects
  - As conversion increases with space time
    - reactant concentration decreases tending to decrease rate
    - temperature increases tending to increase rate
  - Initially expect temperature effect to predominate leading to concave upward shape
  - Eventually concentration must predominate
    - Inflection at point where two effects become equal
    - Concave down beyond that point
- Adiabatic exothermic system always above other curves



Activity 25.2

- The objectives of this activity are
  - Identify two different types of transient responses to a step change in a PFR operating parameter
  - Understand what feature of the step change leads to each type of transient response
  - Examine the duration of the response of a PFR to a step change in one of its operating parameters
- We will use the PFR shown above in a series of thought experiments to qualitatively probe the transient response of a PFR to a set of step changes in operating parameters
  - At the instant shown, the step change has just occurred
  - The green and blue fluid elements are both inside the reactor
    - The green fluid element is the last one to have entered before the step change
    - The blue fluid element entered just before the green one
  - The red and yellow fluid element are both outside the reactor
    - The yellow fluid element will be the first one to enter after the step change
    - The red fluid element will enter right after the yellow one

Duration of the Transient

- There was some unspecified step change right after the green fluid element entered the reactor
- Will the changes that occur in the red fluid element as it moves through the reactor be exactly the same as the changes that occur in the yellow fluid element as it moves through the reactor?
  - Why or why not?
- Once the yellow fluid element has reached the outlet from the reactor, will the changes that occur in the next fluid element to enter the reactor as it moves through the reactor be exactly the same as the changes that occur in the yellow fluid element as it moved through the reactor?
  - Is there a name for this condition
- On the basis of your answers, can you state how long the transient lasted?

Duration of the Transient

- There was some unspecified step change right after the green fluid element entered the reactor
- Will the changes that occur in the red fluid element as it moves through the reactor be exactly the same as the changes that occur in the yellow fluid element as it moves through the reactor? Yes, they will be equal
    - They start at equal compositions, flow at equal rates and experience the same heat transfer with the walls, so there is no difference between them
- Once the yellow fluid element has reached the outlet from the reactor, will the changes that occur in the next fluid element to enter the reactor as it moves through the reactor be exactly the same as the changes that occur in the yellow fluid element as it moved through the reactor? Yes, they will be equal
    - The reasons are the same; note every fluid element now has the same experience; the reactor is at steady state
- On the basis of your answers, can you state how long the transient lasted?
    - The duration of the transient is the amount of time it takes for the yellow fluid element to reach the reactor outlet, and that is equal to the residence time

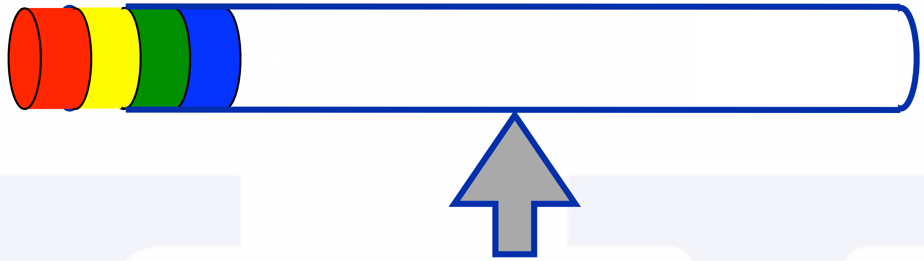
First Step Change

- There was a step change in the inlet composition
- As the green fluid element moves through the reactor, will it experience the exact same changes that the blue element experiences?
  - Why or why not?
- As the yellow fluid element moves through the reactor, will it experience the exact same changes that the green fluid element experiences?
  - Why or why not?
- As the red fluid element moves through the reactor, will it experience the exact same changes that the yellow fluid element experiences?
  - Why or why not?
- What would change if there was a step change in the inlet temperature

First Step Change

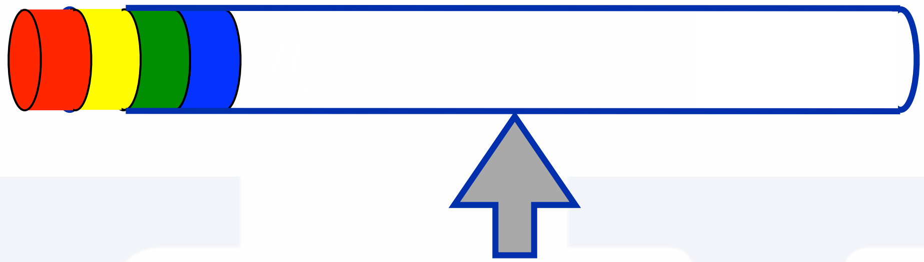
- There was a step change in the inlet composition
- As the green fluid element moves through the reactor, will it experience the exact same changes that the blue element experiences? Yes, they will be equal
  - They started at equal compositions, flow at equal rates and experience the same heat transfer with the walls, so there is no difference between them
- As the yellow fluid element moves through the reactor, will it experience the exact same changes that the green fluid element experiences? No, they will be different
  - The yellow fluid element will be reacting at a different rate than the green due to the composition difference
- As the red fluid element moves through the reactor, will it experience the exact same changes that the yellow fluid element experiences? Yes, they will be equal
  - For the same reason that the blue and green elements are equal
- What would change if there was a step change in the inlet temperature
  - Again, the blue and the green would be equal; the yellow and red would be equal, but the yellow and green would be different.

First Step Change



- Based on the answers you gave on the previous slide, describe what changes you would observe as a function of time if you observed at the point indicated

First Step Change



- Based on the answers you gave on the previous slide, describe what changes you would observe as a function of time if you observed at the point indicated
  - There would be no changes over time until the yellow fluid element reached the observation point
  - When the yellow fluid element reached the observation point, a step change would be observed
  - After the yellow fluid element had reached the observation point, there would be no more changes over time

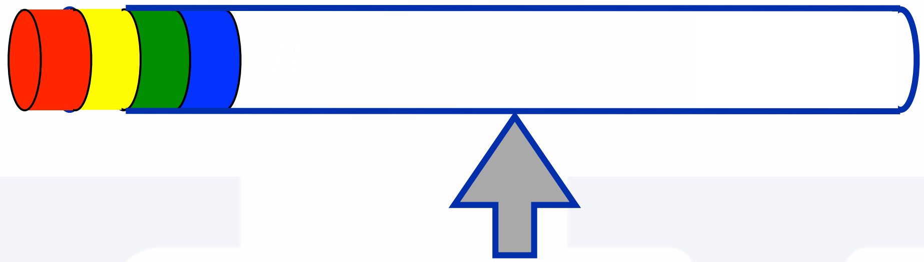
A Different Kind of Step Change

- There was a step change increase in the flow rate
- As the green fluid element moves through the reactor, will it experience the exact same changes that the blue element experiences?
  - Why or why not?
- As the yellow fluid element moves through the reactor, will it experience the exact same changes that the green fluid element experiences?
  - Why or why not?
- As the red fluid element moves through the reactor, will it experience the exact same changes that the yellow fluid element experiences?
  - Why or why not?
- Suppose instead of the flow rate, the temperature of the reactor wall changed (causing a step change in the heat transfer term)?

A Different Kind of Step Change

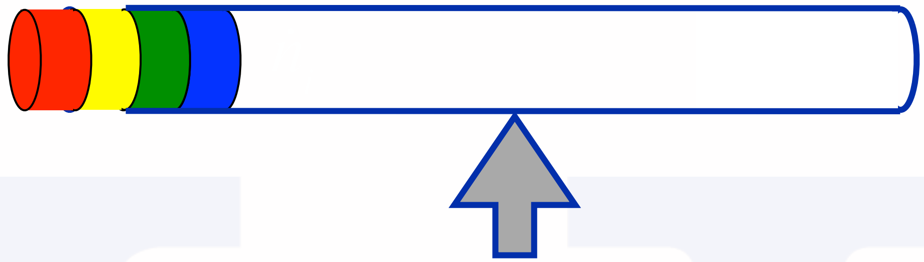
- There was a step change increase in the flow rate
- As the green fluid element moves through the reactor, will it experience the exact same changes that the blue element experiences? No, they will be different
  - When the green element reaches the place where the blue element is, it will not have been in the reactor for as long (due to faster flow), so it will not have reacted as much
- As the yellow fluid element moves through the reactor, will it experience the exact same changes that the green fluid element experiences? No, they will be different
  - The reason is the same
- As the red fluid element moves through the reactor, will it experience the exact same changes that the yellow fluid element experiences? Yes, they will be equal
  - They enter at equal compositions, flow at equal rates and experience the same heat transfer with the walls, so there is no difference between them
- Suppose instead of the flow rate, the temperature of the reactor wall changed (causing a step change in the heat transfer term)? Same answers

Second Step Change



- Based on the answers you gave on the previous slide, describe what changes you would observe as a function of time if you observed at the point indicated
- Compare and contrast the nature of the transient for the preceding case to this case

Second Step Change



- Based on the answers you gave on the previous slide, describe what changes you would observe as a function of time if you observed at the point indicated
  - As soon as the step change was applied, changes would be observed continually until the yellow fluid element reached the observation point
  - After the yellow fluid element had reached the observation point, there would be no more changes over time
- Compare and contrast the nature of the transient for the preceding case to this case
  - In the first case, there will be a step change that moves along the reactor; it will be located at the interface between the green and yellow fluid elements
    - This is sometimes referred to as a "front" moving through the reactor
  - In the second case, there will initially be changes along the whole length of the reactor; as the yellow fluid element moves through, there will be continual changes in front of it, but there will be no changes (at a fixed position) behind it

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
    - 25. Reaction Engineering of PFRs
    - 26. Analysis of Steady State PFRs
    - 27. Analysis of Transient PFRs
  - E. Matching Reactors to Reactions
- Part IV - Non-Ideal Reactions and Reactors