A First Course on Kinetics and Reaction Engineering

Class 11 on Unit 11

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

Laboratory Reactors

- Three models for laboratory reactors used to generate kinetics data when only one reaction is taking place
  - Isothermal batch reactor
    - Critical assumptions are perfect mixing and isothermal
    - $\frac{dn_i}{dt} = Vr_{i,j}$
  - Steady state CSTR
    - Critical assumptions are steady state and perfect mixing
    - $\dot{n}_i - \dot{n}_i^0 = Vr_{i,j}$
  - Isothermal, isobaric, steady state plug flow reactor
    - Critical assumptions are plug flow, steady state, isothermal and isobaric
    - $\frac{d\dot{n}_i}{dz} = \frac{\pi D^2}{4} r_{i,j}$
- The validity of the model equations must be tested before kinetics data are generated and analyzed
  - Some tests don't require reaction to be occurring
    - Flow visualization (smoke tests), extensive instrumentation, measurement of the age function
  - Other tests can be performed while reaction takes place
    - Unit 12

Testing Using the Age Function

- Apply a stimulus at the inlet to the reactor and measure the response at the outlet from the reactor
  - Stimulus may be step change or impulse change in the concentration of a tracer
    - Tracer is something that flows exactly the same as the fluid, but is easily distinguished
    - The stimulus is applied at a point in time, t_0
  - Response is the change in concentration of the tracer in the fluid leaving the reactor over time (after application of the stimulus)
- *F(λ)* ≡ fraction of the fluid leaving a flow system that has been inside the system for a period of time < λ
  - F(0) = 0
  - F(∞) = 1
- Calculation of the age function
  - Using a step change stimulus: $F\left(\lambda = t\right) = \dfrac{w_t - w_0}{w_f - w_0}$
  - Using an impulse stimulus: $F\left(\lambda = t'\right) = \dfrac{\dot{M}\int_{t_0}^{t'}\left(w_{out}\left(t\right) - w_0\right)dt}{m_{tot}}$
    - If the mass of tracer in the impulse was not measured: $m_{tot} = \dot{M}\int_{t_0}^{\infty}\left(w_{out}\left(t\right) - w_0\right)dt$

Testing Using the Age Function

- Expected age functions for reactors that obey the assumptions of the ideal reactor models
  - CSTR: $F_{CSTR}\left(\lambda\right)=1-\exp\left\{\frac{-\lambda}{\bar{t}}\right\}$
  - PFR: $F_{PFR}\left(\lambda\right)=0 \text{ for } \lambda<\bar{t}$

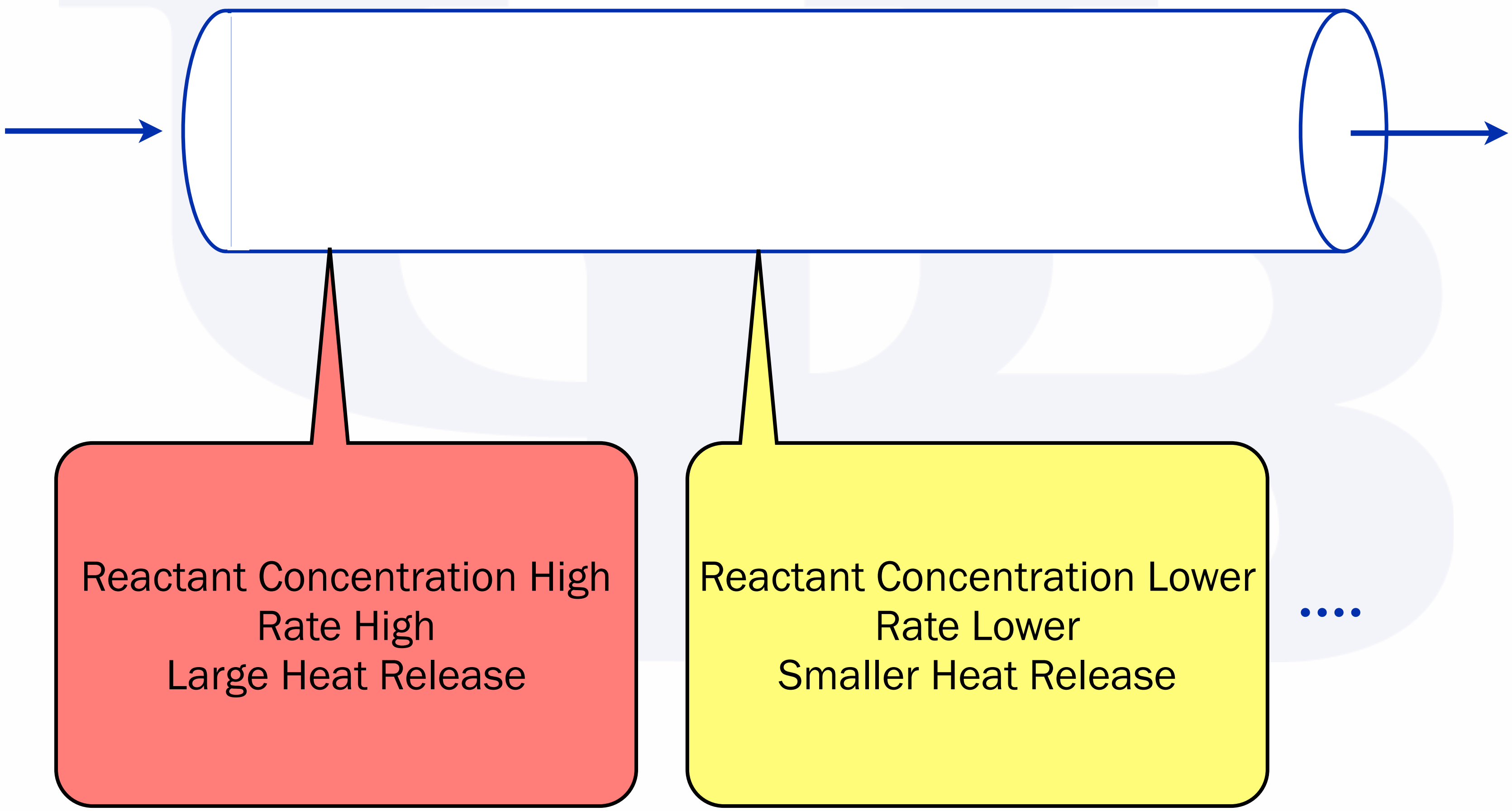
    $F_{PFR}\left(\lambda\right)=1 \text{ for } \lambda\geq\bar{t}$
- Plot $F(\lambda)$ vs. λ and $F_{CSTR}(\lambda)$ (or $F_{PFR}(\lambda)$) vs. λ on the same axes
- Agreement between the measured age function and the ideal reactor age function is a necessary, but not sufficient criterion
  - It confirms that the time scale for mixing is much shorter than the residence time in the reactor
  - It can fail if the time scale for reaction is much shorter than the time scale for mixing

Questions?

Activity 11.1

- Consider a plug flow reactor that you want to be isothermal
  - It's essentially a tube
  - You can add or remove heat through the walls
    - for example, you could flow steam over the outside of the tube to add heat
- The amount of heat released at any point along the reactor is proportional to the rate at that point
  - At the inlet, where the reactant concentration is high, the rate will be high, and lots of heat will be released
  - Farther along the reactor, where the reactant concentration is smaller, the rate will not be as large, and less heat will be released.
  - In other words, the amount of heat that needs to be removed changes continually along the length of the reactor
- How, then, can you configure the system so the reactor is isothermal?
  - If you remove enough heat to cool the inlet to the desired isothermal temperature, then farther down the reactor, the temperature will be below the desired value because too much heat is being removed.
- The same problem occurs with a batch reactor except that there you need to remove more heat at the start of the experiment and less heat later in the experiment
  - How would you do this?

Activity 11.1



Conclusions

- It can be difficult to actually operate a reactor isothermally
  - Need a thermal sink or reservoir
    - Reactor immersed in a stirred oil bath or a fluidized sand bath
    - Reactor tightly fitted within a large block of a metal with a high thermal conductivity (e. g. Al)
      - Metal block heated via oil bath, electrical resistance heaters, etc.
- For this reason, most commercial reactors do not operate isothermally

Practice Problem 11.1

A reactor with a fluid volume of 10 L needs to be tested to determine whether it can be modeled accurately as an ideal CSTR. A steady flow of solvent at 25 L/min is established; there is no tracer in the solvent. Suddenly a valve is opened so that the flow into the reactor contains a tracer at a 3 M concentration. The data at the right were measured following the opening of the valve. Use these data to calculate the value of the age function for each measurement and plot the age function as a function of the fluid "age."

Time (min)	Outlet Tracer Conc. (M)
0	0.00
0.1	0.51
0.2	1.04
0.3	1.50
0.4	1.97
0.5	2.12
0.6	2.46
0.7	2.51
0.8	2.64
0.9	2.75
1	2.78
1.1	2.94
1.2	2.92
1.3	2.90
1.4	2.91
1.5	2.97
1.6	2.98
1.7	3.03
1.8	2.88
1.9	3.01
2	3.04

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