A First Course on Kinetics and Reaction Engineering

Class 17 on Unit 17

Where We're Going

- Part I - Chemical Reactions

- Part II - Chemical Reaction Kinetics

- Part III - Chemical Reaction Engineering
  - A. Ideal Reactors
    - 17. Reactor Models and Reaction Types
  - 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

Reaction Engineering

- Objectives
  - Construct accurate mathematical models of real world reactors
  - Use those models to perform some engineering task
- Tasks
  - Reaction engineering: studies involving an existing reactor
  - Reactor design: specifying a reactor that doesn't yet exist along with its operating procedures
- Real world reaction engineering
  - Maximize the rate of profit realized by operating the overall process (not just the reactor)
  - Integration of the reactor into the overall process may place constraints upon the reactor design and operating conditions
- Generally
  - generate the desired product as fast as possible
  - with the highest selectivity possible
  - using as little energy as possible
  - in as small a reactor volume as possible
  - while maintaining
    - reliability
    - operability
    - environmental compatibility
    - safety

Ideal Reactor Design Equations

Batch Reactor

$$\frac{dn_i}{dt} = V \sum_{\substack{j=all \\ reactions}} \nu_{i,j} r_j$$

$$\dot{Q} - \dot{W} = \frac{dT}{dt} \sum_{\substack{i=all \\ species}} \left(n_i \hat{C}_{pi} \right) + V \sum_{\substack{j=all \\ reactions}} \left(r_j \Delta H_j \right) - \frac{dP}{dt} V - P \frac{dV}{dt}$$

CSTR

$$\frac{\dot{n}_i}{\dot{V}} \frac{dV}{dt} + \frac{V}{\dot{V}} \frac{d\dot{n}_i}{dt} - \frac{\dot{n}_i V}{\dot{V}^2} \frac{d\dot{V}}{dt} = \dot{n}_i^0 - \dot{n}_i + V \sum_{\substack{j=all \\ reactions}} \nu_{i,j} r_j$$

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all \\ species}} \left(\dot{n}_i^0 \int_{T^0}^{T} \hat{C}_{pi} \, dT \right) + V \sum_{\substack{j=all \\ reactions}} \left(r_j \Delta H_j \big|_T \right) + \frac{V}{\dot{V}} \sum_{\substack{i=all \\ species}} \left(\dot{n}_i \hat{C}_{pi} \right) \left(\frac{dT}{dt} \right) - V \left(\frac{dP}{dt} \right) + P \left(\frac{dV}{dt} \right)$$

Ideal Reactor Design Equations

Steady State CSTR

$$0 = \dot{n}_i^0 - \dot{n}_i + V \sum_{\substack{j=all \\ reactions}} \nu_{i,j} r_j$$

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all \\ species}} \left(\dot{n}_i^0 \int_{T^0}^{T} \hat{C}_{pi} \, dT \right) + V \sum_{\substack{j=all \\ reactions}} \left(r_j \Delta H_j \big|_T \right)$$

PFR

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

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

Ideal Reactor Design Equations

Steady State RFR

$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \sum_{\substack{j=all \\ reactions}} \nu_{i,j} r_j$$

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

$$\frac{\partial P}{\partial z} = -\frac{G}{g_c} \left(\frac{4}{\pi D^2} \right) \frac{\partial \dot{V}}{\partial z} - \frac{2 f G^2}{\rho D} \qquad \text{(Unpacked Tube)}$$

$$\frac{\partial P}{\partial z} = -\frac{1-\varepsilon}{\varepsilon^3} \frac{G^2}{\rho \Phi_s D_p g_c} \left[\frac{150(1-\varepsilon)\mu}{\Phi_s D_p G} + 1.75 \right] \qquad \text{(Packed Bed)}$$

Typical Kinetics Behavior and Reaction Classification

- Typical kinetics behavior
  - As T increases, the rate increases
    - final conversion decreases for exothermic; increases for endothermic reactions
  - As concentration or partial pressure of reactants decreases, the rate decreases
  - As the concentration or partial pressure of products increases, the rate decreases for reversible reactions; is not strongly affected for irreversible reactions

- Reaction Classification
  - Auto-thermal reactions: the (exothermic) heat of reaction is sufficiently large to heat the reactants to reaction temperature
  - Auto-catalytic reactions: rate increases as the product concentration increases
  - Reactant Inhibited Reactions: rate decreases as the reactant concentration increases
  - Product Inhibited Reactions: rate decreases as the product concentration increases
  - Parallel Reactions
    - $A \rightarrow B$
    - $A \rightarrow C$
  - Series Reactions
    - $A \rightarrow B$
    - $B \rightarrow C$
  - Series-Parallel Reactions
    - $A + B \rightarrow R + S$
    - $R + B \rightarrow T + S$

Questions?

Exam Procedure

- When you arrive
  - ‣ Place coats, hats, backpacks, etc. along the front or side walls of the room
  - ‣ Take only pencil, eraser and/or pen to your seat
  - ‣ The exam will not begin until everyone is seated

- Once the exam starts, you may not leave the room
  - ‣ If you leave, you must turn in your exam before doing so, and you will not be permitted to resume the exam
  - ‣ Therefore, use the restroom prior to the exam

- The exam will end at 10:50 AM

Solution to the Practice Exam

1. Which of the following is the Arrhenius expression?

a. $K_j = \exp\left\{\dfrac{-\Delta G_j}{RT}\right\}$

b. $k_j = \exp\left\{\dfrac{\Delta S_j}{R}\right\}\exp\left\{\dfrac{-\Delta H_j}{RT}\right\}$

c. $K_j = K_{0,j}\exp\left\{\dfrac{-\Delta H_j}{RT}\right\}$

d. $k_j = k_{0,j}\exp\left(\dfrac{-E_j}{RT}\right)$

e. $k_j = k_{0,j}T^a\exp\left(\dfrac{-E_j}{RT}\right)$

2. True or false? Every mechanism has a rate-determining step.

3. A Lineweaver-Burke plot is (choose all that are true)

   a. a plot of a linearized form of a Michaelis-Menten kinetic expression

   b. used to determine whether the kinetics of an enzyme-catalyzed reaction obey Michaelis-Menten kinetics

   c. used to determine the values of the parameters appearing in a Michaelis-Menten kinetic expression

   d. parabolic in shape with the concave side facing up

   e. parabolic in shape with the concave side facing down

4. The age function is measured by applying a stimulus and measuring a response.

   a. The stimulus is applied at the inlet to the reactor and the response is measured at the inlet to the reactor.

   b. The stimulus is applied at the outlet from the reactor and the response is measured at the outlet from the reactor.

   c. The stimulus is applied at the outlet from the reactor and the response is measured at the inlet to the reactor.

   d. The stimulus is applied at the inlet to the reactor and the response is measured at the outlet from the reactor.

   e. The stimulus can be applied at either the inlet or the outlet of the reactor, and the response is measured at the other location.

5. The limiting values of the age function are

   a. $F(0) = 1$ and $F(1) = \infty$

   b. $F(1) = 0$ and $F(\infty) = \infty$

   c. $F(0) = 1$ and $F(1) = \infty$

   d. $F(0) = 0$ and $F(\infty) = 1$

   e. $F(0) = -\infty$ and $F(1) = \infty$

Problem 1

- Stable species: C_7H_8, Cl_2, C_7H_7Cl and HCl
- Reactive intermediates: Al_2Cl_6, $HCl-AlCl_3-AlCl_3$, $HCl-AlCl_3$, Cl_2-AlCl_3 and $AlCl_4-C_7H_8Cl$
- There is no rate determining step, therefore write rate with respect to a reactant or product
  - ‣ $r_{C_7H_8} = k_{3f}\left[Cl_2 - AlCl_3\right]\left[C_7H_8\right] - k_{3r}\left[AlCl_4 - C_7H_8Cl\right]$ (6)
- Not acceptable, eliminate concentrations of reactive intermediates
  - ‣ Step 1 is equilibrated: $K_1 = \dfrac{\left[Al_2Cl_6\right]\left[HCl\right]}{\left[HCl - AlCl_3 - AlCl_3\right]}$ (1)
  - ‣ Conservation of catalyst: $C_0 = \left[Al_2Cl_6\right] + \left[HCl - AlCl_3 - AlCl_3\right]$
    $$+0.5\left[HCl - AlCl_3\right] + 0.5\left[Cl_2 - AlCl_3\right] + 0.5\left[AlCl_4 C_7H_8Cl\right]$$ (2)
  - ‣ Bodenstein steady state approximation on all but two of the reactive intermediates:

$$0 = k_{3f}\left[Cl_2 - AlCl_3\right]\left[C_7H_8\right] - k_{4f}\left[AlCl_4 - C_7H_8Cl\right]$$ (3)

$$0 = k_{1f}\left[Al_2Cl_6\right]\left[HCl\right] - k_{1r}\left[HCl - AlCl_3 - AlCl_3\right]$$ (4)

$$0 = k_{2f}\left[HCl - AlCl_3 - AlCl_3\right]\left[Cl_2\right] - k_{2r}\left[HCl - AlCl_3\right]\left[Cl_2 - AlCl_3\right]$$
$$+ k_{4f}\left[AlCl_4 - C_7H_8Cl\right] - k_{5f}\left[HCl - AlCl_3\right]\left[Cl_2\right] + k_{5r}\left[Cl_2 - AlCl_3\right]\left[HCl\right]$$ (5)

- Solve equations (1) through (5) simultaneously to get expressions for $[Al_2Cl_6]$, $[HCl–AlCl_3–AlCl_3]$, $[HCl–AlCl_3]$, $[Cl_2–AlCl_3]$ and $[AlCl_4–C_7H_8Cl]$
- Substitute the resulting expressions for $[Cl_2–AlCl_3]$ and $[AlCl_4–C_7H_8Cl]$ into equation (6)

Problem 2

- Let $A = C_3H_6$, $B = C_6H_6$ and $Z = C_9H_{14}$ so $A + B \rightarrow Z$
- Given: $V = 3.27$ L, $T = 500$ K, $P^0 = 340$ mm Hg, and a data set with values of t and P
- Mole balance design equation: $\dfrac{dn_A}{dt} = -kVP_A P_B$
- Eliminate P_A and P_B

$$P_A = \frac{n_A RT}{V} \qquad P_B = \frac{n_B RT}{V} = \frac{\left(n_B^0 - n_A^0 + n_A\right)RT}{V}$$

$$\frac{dn_A}{dt} = -\frac{k(RT)^2}{V} n_A \left(n_B^0 - n_A^0 + n_A\right)$$

- Separate variables and integrate

$$\int_{n_A^0}^{n_A} \frac{dn_A}{n_A \left(n_A^0 - n_B^0 - n_A\right)} = \frac{k(RT)^2}{V}\int_0^t dt \quad \Rightarrow \quad \frac{-1}{n_A^0 - n_B^0}\ln\left[\left(\frac{n_B^0 - n_A^0 + n_A}{n_A}\right)\left(\frac{n_A^0}{n_B^0}\right)\right] = \frac{k(RT)^2}{V}t$$

- Linearize the equation

$$y = \frac{-1}{n_A^0 - n_B^0}\ln\left[\left(\frac{n_B^0 - n_A^0 + n_A}{n_A}\right)\left(\frac{n_A^0}{n_B^0}\right)\right] \qquad x = \frac{(RT)^2}{V}t \qquad y = kx$$

- Fit y = kx to the data by calculating x and y for each data point and then fitting numerically
  - To do so need values for n_A^0, n_B^0 and n_A for each data point

$$n_{tot}^0 = \frac{P^0 V}{RT} \qquad n_A^0 = \frac{2}{3} n_{tot}^0 \qquad n_B^0 = \frac{1}{3} n_{tot}^0$$

$$n_{tot} = \frac{PV}{RT} \qquad n_{tot} = n_{tot}^0 - \xi \quad \Rightarrow \quad \xi = n_{tot}^0 - n_{tot} \qquad n_A = n_A^0 - \xi$$

- Fitting will yield r^2, a model plot and the value of the slope, in this case k with its uncertainty
  - If r^2 is close to 1.0 AND the data in the model plot scatter randomly from the line by a small amount (no systematic deviations), the rate expression is acceptable.

Problem 3

- Given: V = 276 cm³, T = 505 K and a data set including values of P, $\dot{n}_A^0$, $\dot{n}_I^0$ (= $\dot{n}_I$) and $\dot{n}_S$ for each experiment

- Mole balance design equation: $\dot{n}_A - \dot{n}_A^0 = -k_1 V P_A$

- Linearize the equation
  - $y = \dot{n}_A - \dot{n}_A^0$
  - $x = -V P_A$
  - $y = k_1 x$

- Fit y = k_1x to the experimental data by calculating x and y for each data point and then fitting numerically
  - To do so, need $\dot{n}_A$ and P_A for each data point

$$\dot{n}_S = \dot{n}_S^0 + \xi = \xi$$

$$\dot{n}_A = \dot{n}_A^0 - \xi$$

$$P_A = \frac{\dot{n}_A}{\dot{n}_{tot}} P = \frac{\dot{n}_A^0 - \xi}{\dot{n}_A^0 + \dot{n}_I^0 + 2\xi} P$$

- Fitting will yield r², a model plot and the value of the slope, in this case k with its uncertainty
  - If r² is close to 1.0 AND the data in the model plot scatter randomly from the line by a small amount (no systematic deviations), the rate expression is acceptable.

Where We're Going

- Part I - Chemical Reactions

- Part II - Chemical Reaction Kinetics

- Part III - Chemical Reaction Engineering

  ‣ A. Ideal Reactors

    - 17. Reactor Models and Reaction Types

  ‣ B. Perfectly Mixed Batch Reactors

    - 18. Reaction Engineering of Batch Reactors

    - 19. Analysis of Batch Reactors

    - 20. Optimization of Batch Reactor Processes

  ‣ C. Continuous Flow Stirred Tank Reactors

  ‣ D. Plug Flow Reactors

  ‣ E. Matching Reactors to Reactions

- Part IV - Non-Ideal Reactions and Reactors