A First Course on Kinetics and Reaction Engineering

Class 8 on Unit 8

Where We've Been

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
  - A. Rate Expressions
    - 4. Reaction Rates and Temperature Effects
    - 5. Empirical and Theoretical Rate Expressions
    - 6. Reaction Mechanisms
    - 7. The Steady State Approximation
    - 8. Rate Determining Step
    - 9. Homogeneous and Enzymatic Catalysis
    - 10. Heterogeneous Catalysis
  - B. Kinetics Experiments
  - C. Analysis of Kinetics Data
- Part III - Chemical Reaction Engineering
- Part IV - Non-Ideal Reactions and Reactors

Rate-Determining Step

- If there is a step in a reaction mechanism for which the ΔG associated with that step is essentially equal to ΔG for the macroscopically observed, non-elementary reaction (j)
  - That step is called the rate-determining step (rds)
  - The rate of the macroscopically observed, non-elementary reaction is equal to the rate of the rate-determining step

$$r_j = r_{rds} = k_{rds,f} \left(\prod_{\substack{m=\text{all} \\ \text{reactants}}} \left[m \right]^{-\nu_{m,rds}} \right)$$

  - Each of the other steps, *s*, in the mechanism may be assumed to be quasi-equilibrated

$$K_{eq,s} = \prod_{\substack{i\,=\,\text{all} \\ \text{species}}} \left[i \right]^{\nu_{i,s}}$$

- Expressions for the concentrations of the reactive intermediates can be found by writing equilibrium expressions for all steps other than the rate-determining step and solving
- Substitution of these expressions into the rate expression for the non-elementary reaction will eliminate all concentrations (or partial pressures) of reactive intermediates

Questions?

Activity 8.1

- The pile of playing cards in the front of the room represents the reactants in a non-elementary reaction
- I need four volunteers who will represent mechanistic reaction steps
  - To be a reaction step you must take a card from the pile representing your reactant and put it on the pile representing your product
  - The steps they represent will be as follows
    - Reactant to Intermediate 1
    - Intermediate 1 back to reactant (there must be at least 3 cards in the pile)
    - Intermediate 1 to intermediate 2 (rate-determining; no reverse step)
    - Intermediate 2 to product
- The pile representing the first reactive intermediate will be right next to the pile representing the reactants
- The pile representing the second reactive intermediate will be in the back corner of the room
- The pile representing the product will be right next to the pile representing the second intermediate
- I need volunteers to count the number of times the rate-determining step occurs and to count the number of time product is formed

Activity 8.2

Consider the non-elementary reaction given in equation (1). Suppose the mechanism is given by reactions (2) through (4). Generate an expression for the rate of reaction (1) (a) if step (2) is rate-determining, (b) if step (3) is rate-determining and (c) if step (4) is rate determining. Compare the results to a rate expression generated using the Bodenstein steady state approximation.

- Overall (macroscopically observed) reaction

$$2\,A + 2\,B \rightleftarrows Y + 2\,Z \qquad (1)$$

- Mechanism

$$2\,A \rightleftarrows I \qquad (2)$$

$$B + I \rightleftarrows Y + J \qquad (3)$$

$$B + J \rightleftarrows 2\,Z \qquad (4)$$

Solution Procedure

- Check that the mechanism is valid
- List the stable species and the reactive intermediates
- Set the rate of the overall reaction equal to the forward rate of the rate-determining step
  - If the rate expression does not contain reactive intermediates, you are done
- Write equilibrium expressions for all other steps
- Solve the equilbrium expressions to get expressions for the concentrations of the reactive intermediates
- Substitute the expressions for the reactive intermediate concentrations into the rate expression and simplify

Check that the Mechanism is Valid

- Overall (macroscopically observed) reaction

$$2\,A + 2\,B \rightleftarrows Y + 2\,Z \qquad (1)$$

- Mechanism

$$2\,A \rightleftarrows I \qquad (2)$$

$$B + I \rightleftarrows Y + J \qquad (3)$$

$$B + J \rightleftarrows 2\,Z \qquad (4)$$

- Adding the three steps gives the overall reaction, so the mechanism is valid
- Identify the stable species and the reactive intermediates

Check that the Mechanism is Valid

- Overall (macroscopically observed) reaction

  $$2\,A + 2\,B \rightleftarrows Y + 2\,Z \qquad (1)$$

- Mechanism

  $$2\,A \rightleftarrows I \qquad (2)$$

  $$B + I \rightleftarrows Y + J \qquad (3)$$

  $$B + J \rightleftarrows 2\,Z \qquad (4)$$

- Adding the three steps gives the overall reaction, so the mechanism is valid
- Identify the stable species and the reactive intermediates
  - Stable species: A, B, Y and Z
  - Reactive intermediates: I and J

Identify the Stable Species and Reactive Intermediates

- Overall (macroscopically observed) reaction

  $$2\,A + 2\,B \rightleftarrows Y + 2\,Z \qquad (1)$$

- Mechanism

  $$2\,A \rightleftarrows I \qquad (2)$$

  $$B + I \rightleftarrows Y + J \qquad (3)$$

  $$B + J \rightleftarrows 2\,Z \qquad (4)$$

- Adding the three steps gives the overall reaction, so the mechanism is valid
- Identify the stable species and the reactive intermediates
  - Stable species: A, B, Y and Z
  - Reactive intermediates: I and J
- With reaction 2 as RDS, set the rate of the overall reaction equal to the forward rate of reaction (2)
  - If the rate expression does not contain reactive intermediates, you are done

Reaction (2) Rate-Determining

- Overall (macroscopically observed) reaction

  2 A + 2 B ⇄ Y + 2 Z (1)

- Mechanism

  2 A ⇄ I (2)

  B + I ⇄ Y + J (3)

  B + J ⇄ 2 Z (4)

$$r_1 = r_{rds} = r_2 = k_{2,f} \left(\prod_{\substack{m=\text{all} \\ \text{reactants}}} \left[m \right]^{-\nu_{m,rds}} \right) = k_{2,f} \left[A \right]^2$$

$$r_1 k_{2,f} \left[A \right]^2$$

Identify the Stable Species and Reactive Intermediates

- Overall (macroscopically observed) reaction

  $$2\,A + 2\,B \rightleftarrows Y + 2\,Z \qquad (1)$$

- Mechanism

  $$2\,A \rightleftarrows I \qquad (2)$$

  $$B + I \rightleftarrows Y + J \qquad (3)$$

  $$B + J \rightleftarrows 2\,Z \qquad (4)$$

- Adding the three steps gives the overall reaction, so the mechanism is valid
- Identify the stable species and the reactive intermediates
  - Stable species: A, B, Y and Z
  - Reactive intermediates: I and J
- With reaction 3 as RDS, set the rate of the overall reaction equal to the forward rate of reaction (2)
  - If the rate expression does not contain reactive intermediates, you are done

Identify the Stable Species and Reactive Intermediates

- Overall (macroscopically observed) reaction

  2 A + 2 B ⇄ Y + 2 Z (1)

- Mechanism

  2 A ⇄ I (2)

  B + I ⇄ Y + J (3)

  B + J ⇄ 2 Z (4)

- Adding the three steps gives the overall reaction, so the mechanism is valid
- Identify the stable species and the reactive intermediates
  - Stable species: A, B, Y and Z
  - Reactive intermediates: I and J
- With reaction 3 as RDS, set the rate of the overall reaction equal to the forward rate of reaction (2)
  - If the rate expression does not contain reactive intermediates, you are done

$$r_j = r_{rds} = k_{rds,f}\left(\prod_{\substack{m=\text{all}\\ \text{reactants}}}\left[m\right]^{-\nu_{m,rds}}\right) \quad \Rightarrow \quad r_1 = k_{3,f}\left[B\right]\left[I\right]$$

Write Equilibrium Expressions for the Other Steps

- Overall (macroscopically observed) reaction

  $2\,A + 2\,B \rightleftarrows Y + 2\,Z$ (1)

- Mechanism

  $2\,A \rightleftarrows I$ (2)

  $B + I \rightleftarrows Y + J$ (3)

  $B + J \rightleftarrows 2\,Z$ (4)

$$r_j = r_{rds} = k_{rds,f}\left(\prod_{\substack{m=\text{all}\\ \text{reactants}}}\left[m\right]^{-\nu_{m,rds}}\right) \quad \Rightarrow \quad r_1 = k_{3,f}\left[B\right]\left[I\right]$$

- Write equilibrium expressions for the other steps, solve to get expressions for the concentrations of the reactive intermediates and substitute in the rate expression

Write Equilibrium Expressions for the Other Steps

- Overall (macroscopically observed) reaction

  2 A + 2 B ⇄ Y + 2 Z (1)

- Mechanism

  2 A ⇄ I (2)

  B + I ⇄ Y + J (3)

  B + J ⇄ 2 Z (4)

$$r_j = r_{rds} = k_{rds,f}\left(\prod_{\substack{m=\text{all}\\ \text{reactants}}} \left[m\right]^{-\nu_{m,rds}}\right) \quad \Rightarrow \quad r_1 = k_{3,f}\left[B\right]\left[I\right]$$

$$K_{eq,2} = \frac{\left[I\right]}{\left[A\right]^2} \quad \Rightarrow \quad \left[I\right] = K_{eq,2}\left[A\right]^2$$

$$r_1 = k_{3,f}K_{eq,2}\left[A\right]^2\left[B\right]$$

Reaction (4) Rate-Determining

- Overall (macroscopically observed) reaction

  $$2\,A + 2\,B \rightleftarrows Y + 2\,Z \qquad (1)$$

- Mechanism

  $$2\,A \rightleftarrows I \qquad (2)$$

  $$B + I \rightleftarrows Y + J \qquad (3)$$

  $$B + J \rightleftarrows 2\,Z \qquad (4)$$

Reaction (4) Rate-Determining

- Overall (macroscopically observed) reaction

  2 A + 2 B ⇄ Y + 2 Z (1)

- Mechanism

  2 A ⇄ I (2)

  B + I ⇄ Y + J (3)

  B + J ⇄ 2 Z (4)

$$r_j = r_{rds} = k_{rds,f}\left(\prod_{\substack{m=\text{all}\\ \text{reactants}}}\left[m\right]^{-\nu_{m,rds}}\right) \quad \Rightarrow \quad r_1 = k_{4,f}\left[B\right]\left[J\right]$$

$$K_{eq,2} = \frac{\left[I\right]}{\left[A\right]^2}\ ;\ K_{eq,3} = \frac{\left[Y\right]\left[J\right]}{\left[B\right]\left[I\right]} \quad \Rightarrow \quad \left[I\right] = K_{eq,2}\left[A\right]^2\ ;\ \left[J\right] = \frac{K_{eq,2}K_{eq,3}\left[A\right]^2\left[B\right]}{\left[Y\right]}$$

$$r_1 = k_{4,f}K_{eq,2}K_{eq,3}\frac{\left[A\right]^2\left[B\right]^2}{\left[Y\right]}$$

Use the Bodenstein Steady State Approximation

- Overall (macroscopically observed) reaction

  $$2\,A + 2\,B \rightleftarrows Y + 2\,Z \qquad (1)$$

- Mechanism

  $$2\,A \rightleftarrows I \qquad (2)$$

  $$B + I \rightleftarrows Y + J \qquad (3)$$

  $$B + J \rightleftarrows 2\,Z \qquad (4)$$

Bodenstein Steady State Approximation

$$r_{Y,1} = r_1 = k_{3,f}\left[B\right]\left[I\right] - k_{3,r}\left[Y\right]\left[J\right]$$

$$0 = k_{2,f}\left[A\right]^2 - k_{2,r}\left[I\right] - k_{3,f}\left[B\right]\left[I\right] + k_{3,r}\left[Y\right]\left[J\right]$$

$$0 = k_{3,f}\left[B\right]\left[I\right] - k_{3,r}\left[Y\right]\left[J\right] - k_{4,f}\left[B\right]\left[J\right] + k_{4r}\left[Z\right]^2$$

$$\left[I\right] = \frac{k_{2,f}k_{4,r}\left[A\right]^2\left[B\right] + k_{2,f}k_{3,r}\left[A\right]^2\left[Y\right] + k_{3,r}k_{4,r}\left[Y\right]\left[Z\right]^2}{k_{3,f}k_{4,r}\left[B\right]^2 + k_{2,r}k_{4,r}\left[B\right] + k_{2,r}k_{3,r}\left[Y\right]}$$

$$\left[J\right] = \frac{k_{2,f}k_{3,f}\left[A\right]^2\left[B\right] + k_{3,f}k_{4,r}\left[B\right]\left[Z\right]^2 + k_{2,r}k_{4,r}\left[Z\right]^2}{k_{3,f}k_{4,r}\left[B\right]^2 + k_{2,r}k_{4,r}\left[B\right] + k_{2,r}k_{3,r}\left[Y\right]}$$

$$r = \frac{k_{2,f}k_{3,f}k_{4,r}\left[A\right]^2\left[B\right]^2 - k_{2,r}k_{3,r}k_{4,r}\left[Y\right]\left[Z\right]^2}{k_{3,f}k_{4,r}\left[B\right]^2 + k_{2,r}k_{4,r}\left[B\right] + k_{2,r}k_{3,r}\left[Y\right]}$$

Comparison

- Rate-determining step rate expressions

$$r_1 k_{2,f}\left[A\right]^2 \qquad r_1 = k_{3,f}K_{eq,2}\left[A\right]^2\left[B\right] \qquad r_1 = k_{4,f}K_{eq,2}K_{eq,3}\frac{\left[A\right]^2\left[B\right]^2}{\left[Y\right]}$$

- Bodenstein steady state approximation rate expression

$$r = \frac{k_{2,f}k_{3,f}k_{4,r}\left[A\right]^2\left[B\right]^2 - k_{2,r}k_{3,r}k_{4,r}\left[Y\right]\left[Z\right]^2}{k_{3,f}k_{4,r}\left[B\right]^2 + k_{2,r}k_{4,r}\left[B\right] + k_{2,r}k_{3,r}\left[Y\right]}$$

- Bodenstein expression neglecting reverse rate

$$r = \frac{k_{2,f}k_{3,f}k_{4,r}\left[A\right]^2\left[B\right]^2}{k_{3,f}k_{4,r}\left[B\right]^2 + k_{2,r}k_{4,r}\left[B\right] + k_{2,r}k_{3,r}\left[Y\right]}$$

- Notice the three rate-determining step rate expressions are limiting cases of the Bodenstein expression neglecting the reverse reaction with one of the three terms in the denominator predominating
    - Therefore, if there is a rate-determining step, the Bodenstein steady state approximation will also yield a valid rate expression
    - Put differently, the Bodenstein steady state approximation is consistent with, but more rigorous than, assuming a rate-determining step

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