A First Course on Kinetics and Reaction Engineering

Class 7 on Unit 7

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

Mechanistic Rate Expressions

$$r_{i,j} = \sum_{\substack{s=\text{ all}\\ \text{steps}}} \nu_{i,s} \left(k_{s,f} \prod_{\substack{m=\text{all}\\ \text{reactants}}} [m]^{-\nu_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all}\\ \text{products}}} [n]^{\nu_{n,s}} \right)$$

- If a mechanistic step is kinetically insignificant, delete the terms that correspond to its rate
- If a mechanistic step is effectively irreversible, delete the term that corresponds to its reverse rate
- Apply Bodenstein steady state approximation to each reactive intermediate
  - $$0 = \sum_{\substack{s=\text{ all}\\ \text{steps}}} \nu_{i,s} \left(k_{s,f} \prod_{\substack{m=\text{all}\\ \text{reactants}}} [m]^{-\nu_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all}\\ \text{products}}} [n]^{\nu_{n,s}} \right)$$
- Solve the resulting set of equations to obtain expressions for the concentrations of the reactive intermediates in terms of concentrations of stable species and rate coefficients from the reaction mechanism
  - Substitute these expressions into the mechanistic rate expression

Questions?

The Bodenstein Steady State Approximation

From a macroscopic point of view, the decomposition of N_2O_5 appears to proceed according to equation (1). In actuality, that reaction is non-elementary. Suppose that the mechanism is given by reactions (2) through (4), where reaction (2) is reversible, but reactions (3) and (4) are irreversible. Using the Bodenstein steady state approximation, derive a rate expression for reaction (1) with respect to O_2. The rate expression should not contain concentrations of reactive intermediates.

$$2\ N_2O_5 \rightleftarrows 4\ NO_2 + O_2 \qquad (1)$$

$$N_2O_5 \rightleftarrows NO_2 + NO_3 \qquad (2)$$

$$NO_2 + NO_3 \rightarrow NO_2 + NO + O_2 \qquad (3)$$

$$NO + NO_3 \rightarrow 2\ NO_2 \qquad (4)$$

Approach

- Check that the mechanism is valid
- Identify the stable species and the reactive intermediates
- Write an expression for the overall rate with respect to one of the reactants or products of the apparent overall reaction
  - Simplify the rate expression if any of the steps are kinetically insignificant or effectively irreversible
- Write the Bodenstein steady state approximation for each reactive intermediate
  - Simplify the equations if any of the steps are kinetically insignificant or effectively irreversible
  - Solve the resulting equations to get expressions for the concentrations (or partial pressures) of each of the reactive intermediates
  - The resulting expressions should only contain rate coefficients and concentrations of stable species
- Anywhere that the concentration of a reactive intermediate appears in the rate expression for the overall reaction, substitute the expression for it that resulted from applying the Bodenstein steady state approximation
- Simplify, if possible

Check that the Mechanism is Valid

- Macroscopically observed reaction

$$2\ N_2O_5 \rightleftarrows 4\ NO_2 + O_2 \qquad (1)$$

- Proposed mechanism

$$N_2O_5 \rightleftarrows NO_2 + NO_3 \qquad (2)$$

$$NO_2 + NO_3 \rightarrow NO_2 + NO + O_2 \qquad (3)$$

$$NO + NO_3 \rightarrow 2\ NO_2 \qquad (4)$$

Identify the Stable Species and the Reactive Intermediates

- Macroscopically observed rection

  $2\ N_2O_5 \rightleftarrows 4\ NO_2 + O_2$ (1)

- Proposed mechanism

  $N_2O_5 \rightleftarrows NO_2 + NO_3$ (2)

  $NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$ (3)

  $NO + NO_3 \rightarrow 2\ NO_2$ (4)

- The mechanism is valid
  - Reaction (1) = 2 x reaction (2) + reaction (3) + reaction (4)

Write an Expression for the Overall Rate and Simplify it, if Possible

- Macroscopically observed rection

  $2\ N_2O_5 \rightleftarrows 4\ NO_2 + O_2$ (1)

- Proposed mechanism

  $N_2O_5 \rightleftarrows NO_2 + NO_3$ (2)

  $NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$ (3)

  $NO + NO_3 \rightarrow 2\ NO_2$ (4)

- The mechanism is valid
  - Reaction (1) = 2 x reaction (2) + reaction (3) + reaction (4)
- The reactive intermediates are NO and NO_3

Apply the Bodenstein Steady State Approximation to the Reactive Intermediates and Simplify

- Macroscopically observed reaction

  $2\ N_2O_5 \rightleftarrows 4\ NO_2 + O_2$ (1)

- Proposed mechanism

  $N_2O_5 \rightleftarrows NO_2 + NO_3$ (2)

  $NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$ (3)

  $NO + NO_3 \rightarrow 2\ NO_2$ (4)

- The mechanism is valid
  - Reaction (1) = 2 x reaction (2) + reaction (3) + reaction (4)
- The reactive intermediates are NO and NO_3
- Overall rate with respect to O_2
  - $r_{O_2,1} = \left(k_{3,f}\left[NO_2\right]\left[NO_3\right] - k_{3,r}\left[NO_2\right]\left[NO\right]\left[O_2\right]\right)$
- Reactions (3) and (4) are irreversible, so the terms associated with their reverse rate can be deleted
  - $r_{O_2,1} = k_{3,f}\left[NO_2\right]\left[NO_3\right]$
- This rate expression is not acceptable because the concentration of NO_3, a reactive intermediate, appears in it

Solve for Expressions for the Reactive Intermediates

- Bodenstein steady state approximation for NO and NO_3
  - $0=\left(k_{3,f}\left[NO_2\right]\left[NO_3\right]-k_{3,r}\left[NO_2\right]\left[NO\right]\left[O_2\right]\right)-\left(k_{4,f}\left[NO\right]\left[NO_3\right]-k_{4,r}\left[NO_2\right]^2\right)$
  - $0=\left(k_{2,f}\left[N_2O_5\right]-k_{2,r}\left[NO_2\right]\left[NO_3\right]\right)-\left(k_{3,f}\left[NO_2\right]\left[NO_3\right]-k_{3,r}\left[NO_2\right]\left[NO\right]\left[O_2\right]\right)$
    $-\left(k_{4,f}\left[NO\right]\left[NO_3\right]-k_{4,r}\left[NO_2\right]^2\right)$
- Reactions (3) and (4) are irreversible, so the terms associated with their reverse rate can be deleted
  - $0=k_{3,f}\left[NO_2\right]\left[NO_3\right]-k_{4,f}\left[NO\right]\left[NO_3\right]$
  - $0=k_{2,f}\left[N_2O_5\right]-k_{2,r}\left[NO_2\right]\left[NO_3\right]-k_{3,f}\left[NO_2\right]\left[NO_3\right]-k_{4,f}\left[NO\right]\left[NO_3\right]$

Substitute into the Overall Rate Expression

- Bodenstein steady state approximation for NO and NO_3
  - $$0=\left(k_{3,f}[NO_2][NO_3]-k_{3,r}[NO_2][NO][O_2]\right)-\left(k_{4,f}[NO][NO_3]-k_{4,r}[NO_2]^2\right)$$
  - $$0=\left(k_{2,f}[N_2O_5]-k_{2,r}[NO_2][NO_3]\right)-\left(k_{3,f}[NO_2][NO_3]-k_{3,r}[NO_2][NO][O_2]\right)-\left(k_{4,f}[NO][NO_3]-k_{4,r}[NO_2]^2\right)$$
- Reactions (3) and (4) are irreversible, so the terms associated with their reverse rate can be deleted
  - $$0=k_{3,f}[NO_2][NO_3]-k_{4,f}[NO][NO_3]$$
  - $$0=k_{2,f}[N_2O_5]-k_{2,r}[NO_2][NO_3]-k_{3,f}[NO_2][NO_3]-k_{4,f}[NO][NO_3]$$
- Solving for the concentrations of NO and NO_3
  - $$[NO]=\frac{k_{3,f}}{k_{4,f}}[NO_2]$$
  - $$[NO_3]=\frac{k_{2,f}[N_2O_5]}{\left(k_{2,r}+2k_{3,f}\right)[NO_2]}$$

Solution

- Bodenstein steady state approximation for NO and NO_3
  - $0 = \left(k_{3,f}[NO_2][NO_3] - k_{3,r}[NO_2][NO][O_2]\right) - \left(k_{4,f}[NO][NO_3] - k_{4,r}[NO_2]^2\right)$
  - $0 = \left(k_{2,f}[N_2O_5] - k_{2,r}[NO_2][NO_3]\right) - \left(k_{3,f}[NO_2][NO_3] - k_{3,r}[NO_2][NO][O_2]\right)$
    $-\left(k_{4,f}[NO][NO_3] - k_{4,r}[NO_2]^2\right)$
- Reactions (3) and (4) are irreversible, so the terms associated with their reverse rate can be deleted
  - $0 = k_{3,f}[NO_2][NO_3] - k_{4,f}[NO][NO_3]$
  - $0 = k_{2,f}[N_2O_5] - k_{2,r}[NO_2][NO_3] - k_{3,f}[NO_2][NO_3] - k_{4,f}[NO][NO_3]$
- Solving for the concentrations of NO and NO_3
  - $[NO] = \dfrac{k_{3,f}}{k_{4,f}}[NO_2]$
  - $[NO_3] = \dfrac{k_{2,f}[N_2O_5]}{\left(k_{2,r} + 2k_{3,f}\right)[NO_2]}$
- Substituting into the rate expression
  - $r_{O_2,1} = k_{3,f}[NO_2][NO_3] = \dfrac{k_{2,f}k_{3,f}}{\left(k_{2,r} + 2k_{3,f}\right)}[N_2O_5]$

Non-Elementary Rate Expressions with Respect to Different Species

$H_2 + Br_2 \rightleftarrows 2\ HBr$ (1)

- Mechanism

  $Br_2 \rightleftarrows 2\ Br\bullet$ (2)

  $Br\bullet + H_2 \rightleftarrows HBr + H\bullet$ (3)

  $H\bullet + Br_2 \rightleftarrows HBr + Br\bullet$ (4)

  $2\ H\bullet \rightleftarrows H_2$ (5)

- In Example 7.1 the rate of reaction (1) with respect to H_2 was used
  - Simplified assuming step (4) to be effectively irreversible and step 5 to be kinetically insignificant
  - Applied the Bodenstein steady state approximation to $Br\bullet$ and $H\bullet$

$$P_{H\bullet} = \frac{k_{3,f} P_{H_2} \sqrt{\dfrac{k_{2,f} P_{Br_2}}{k_{2,r}}}}{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}} \qquad P_{Br\bullet} = \sqrt{\frac{k_{2,f} P_{Br_2}}{k_{2,r}}}$$

  - Final rate expression after substitution:

$$r_{H_2,1} = -\frac{k_{3,f} k_{4,f} \sqrt{\dfrac{k_{2,f}}{k_{2,r}}} P_{H_2} P_{Br_2}^{3/2}}{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}}$$

- Half of the class will repeat only using the rate of reaction (1) with respect to Br_2 and half using the rate of reaction (1) with respect to HBr

Final Rate Expressions are Identical

- The Bodenstein steady state approximation does not change, so the expressions for the partial pressures of Br• and H• remain the same

$$P_{H\bullet} = \frac{k_{3,f} P_{H_2} \sqrt{\frac{k_{2,f} P_{Br_2}}{k_{2,r}}}}{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}} \qquad P_{Br\bullet} = \sqrt{\frac{k_{2,f} P_{Br_2}}{k_{2,r}}}$$

- Rates with respect to Br_2 and HBr (after simplification for irreversible and insignificant steps)

$$r_{Br_2,1} = -\left(k_{2,f} P_{Br_2} - k_{2,r} P_{Br\bullet}^2\right) - \left(k_{4,f} P_{H\bullet} P_{Br_2}\right)$$

$$r_{HBr,1} = \left(k_{3,f} P_{Br\bullet} P_{H_2} - k_{3,r} P_{HBr} P_{H\bullet}\right) + \left(k_{4,f} P_{H\bullet} P_{Br_2}\right)$$

- After substitution of the Bodenstein steady state approximation expressions for the concentrations of the reactive intermediates

$$r_1 = \frac{r_{H_2,1}}{-1} = \frac{r_{Br_2,1}}{-1} = \frac{r_{HBr,1}}{2} = \frac{k_{3,f} k_{4,f} \sqrt{\frac{k_{2,f}}{k_{2,r}}} P_{H_2} P_{Br_2}^{3/2}}{k_{3,r} P_{HBr} + k_{4,f} P_{Br_2}}$$

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