The background features a large, stylized blue and grey buffalo mascot. The buffalo is facing forward with its mouth open, showing its teeth and tongue. Below the buffalo's head, the word "BUFFALO" is written in a large, bold, white, italicized font with a grey outline. The text is positioned across the lower half of the image.

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
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 - ▶ B. Kinetics Experiments
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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

$$\triangleright 0 = \sum_{\substack{s = \text{all} \\ \text{steps}}} \nu_{i,s} \left(k_{s,f} \prod_{\substack{m = \text{all} \\ \text{reactants}}} [m]^{-\nu_{m,s}} - k_{s,r} \prod_{\substack{n = \text{all} \\ \text{products}}} [n]^{\nu_{n,s}} \right)$$

- 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

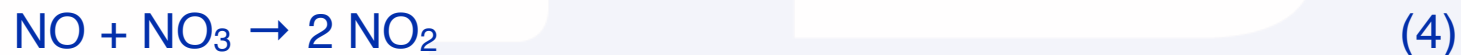
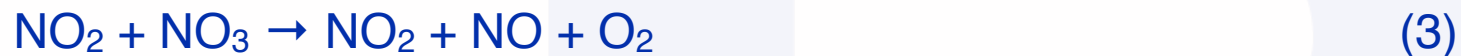
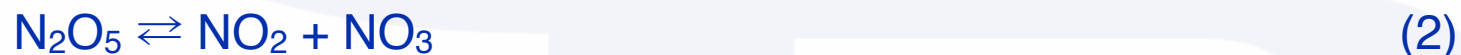
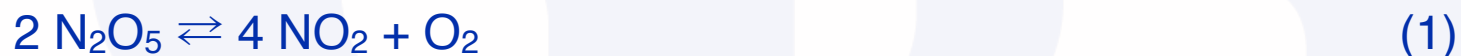


Questions?



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.



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

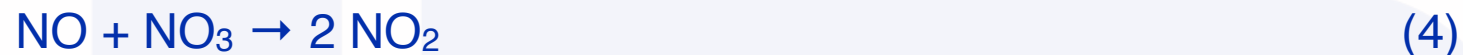


Check that the Mechanism is Valid

- Macroscopically observed reaction



- Proposed mechanism

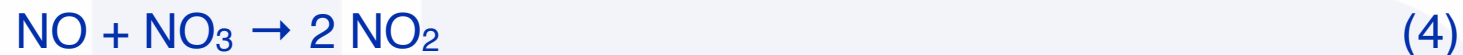


Identify the Stable Species and the Reactive Intermediates

- Macroscopically observed reaction



- Proposed mechanism



- The mechanism is valid

- ▶ Reaction (1) = 2 x reaction (2) + reaction (3) + reaction (4)

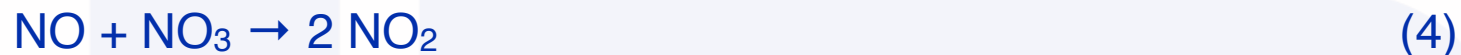


Write an Expression for the Overall Rate and Simplify it, if Possible

- Macroscopically observed reaction



- Proposed mechanism



- The mechanism is valid

▸ Reaction (1) = 2 x reaction (2) + reaction (3) + reaction (4)

- The reactive intermediates are NO and NO₃

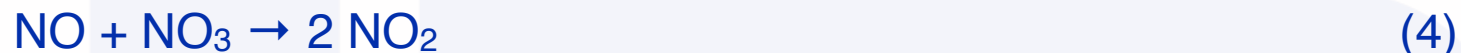


Apply the Bodenstein Steady State Approximation to the Reactive Intermediates and Simplify

- Macroscopically observed reaction



- Proposed mechanism



- The mechanism is valid

‣ Reaction (1) = 2 x reaction (2) + reaction (3) + reaction (4)

- The reactive intermediates are NO and NO₃

- Overall rate with respect to O₂

$$\text{‣ } r_{\text{O}_2,1} = (k_{3,f} [\text{NO}_2][\text{NO}_3] - k_{3,r} [\text{NO}_2][\text{NO}][\text{O}_2])$$

- Reactions (3) and (4) are irreversible, so the terms associated with their reverse rate can be deleted

$$\text{‣ } r_{\text{O}_2,1} = k_{3,f} [\text{NO}_2][\text{NO}_3]$$

- This rate expression is not acceptable because the concentration of NO₃, a reactive intermediate, appears in it



Solve for Expressions for the Reactive Intermediates

- Bodenstein steady state approximation for NO and NO₃
 - $0 = (k_{3,f} [NO_2][NO_3] - k_{3,r} [NO_2][NO][O_2]) - (k_{4,f} [NO][NO_3] - k_{4,r} [NO_2]^2)$
 - $0 = (k_{2,f} [N_2O_5] - k_{2,r} [NO_2][NO_3]) - (k_{3,f} [NO_2][NO_3] - k_{3,r} [NO_2][NO][O_2]) - (k_{4,f} [NO][NO_3] - k_{4,r} [NO_2]^2)$
- Reactions (3) and (4) are irreversible, so the terms associated with their reverse rate can be deleted
 - $0 = k_{3,f} [NO_2][NO_3] - k_{4,f} [NO][NO_3]$
 - $0 = k_{2,f} [N_2O_5] - k_{2,r} [NO_2][NO_3] - k_{3,f} [NO_2][NO_3] - k_{4,f} [NO][NO_3]$



Substitute into the Overall Rate Expression

- Bodenstein steady state approximation for NO and NO₃
 - $0 = (k_{3,f} [NO_2][NO_3] - k_{3,r} [NO_2][NO][O_2]) - (k_{4,f} [NO][NO_3] - k_{4,r} [NO_2]^2)$
 - $0 = (k_{2,f} [N_2O_5] - k_{2,r} [NO_2][NO_3]) - (k_{3,f} [NO_2][NO_3] - k_{3,r} [NO_2][NO][O_2]) - (k_{4,f} [NO][NO_3] - k_{4,r} [NO_2]^2)$
- 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 NO₃
 - $[NO] = \frac{k_{3,f}}{k_{4,f}} [NO_2]$
 - $[NO_3] = \frac{k_{2,f} [N_2O_5]}{(k_{2,r} + 2k_{3,f}) [NO_2]}$



Solution

- Bodenstein steady state approximation for NO and NO₃
 - $0 = (k_{3,f} [NO_2][NO_3] - k_{3,r} [NO_2][NO][O_2]) - (k_{4,f} [NO][NO_3] - k_{4,r} [NO_2]^2)$
 - $0 = (k_{2,f} [N_2O_5] - k_{2,r} [NO_2][NO_3]) - (k_{3,f} [NO_2][NO_3] - k_{3,r} [NO_2][NO][O_2]) - (k_{4,f} [NO][NO_3] - k_{4,r} [NO_2]^2)$
- 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 NO₃
 - $[NO] = \frac{k_{3,f}}{k_{4,f}} [NO_2]$
 - $[NO_3] = \frac{k_{2,f} [N_2O_5]}{(k_{2,r} + 2k_{3,f}) [NO_2]}$
- Substituting into the rate expression
 - $r_{O_2,1} = k_{3,f} [NO_2][NO_3] = \frac{k_{2,f} k_{3,f}}{(k_{2,r} + 2k_{3,f})} [N_2O_5]$



Non-Elementary Rate Expressions with Respect to Different Species



- Mechanism



- 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 $\text{Br}\cdot$ and $\text{H}\cdot$

$$P_{\text{H}\cdot} = \frac{k_{3,f} P_{\text{H}_2} \sqrt{\frac{k_{2,f} P_{\text{Br}_2}}{k_{2,r}}}}{k_{3,r} P_{\text{HBr}} + k_{4,f} P_{\text{Br}_2}} \quad P_{\text{Br}\cdot} = \sqrt{\frac{k_{2,f} P_{\text{Br}_2}}{k_{2,r}}}$$

- ▶ Final rate expression after substitution:
$$r_{\text{H}_2,1} = - \frac{k_{3,f} k_{4,f} \sqrt{\frac{k_{2,f}}{k_{2,r}}} P_{\text{H}_2} P_{\text{Br}_2}^{3/2}}{k_{3,r} P_{\text{HBr}} + k_{4,f} P_{\text{Br}_2}}$$

- 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

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

$$P_{Br\cdot} = \sqrt{\frac{k_{2,f} P_{Br_2}}{k_{2,r}}}$$

- Rates with respect to Br₂ and HBr (after simplification for irreversible and insignificant steps)

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

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

- 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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