Reaction Mechanisms

Reaction Mechanisms

The Big Picture

- Our goal for today is to develop a system for verifying reaction mechanisms, using a two step evaluation process...
  1. Do the elementary steps sum to the subject reaction?
  2. Is the rate law for the rate determining elementary step the rate law for the subject reaction?

Reaction Order

Reaction Mechanisms

- $A + B \Longrightarrow C$
  - $A \Longrightarrow A_1 + A_2$
  - $A_1 + B \Longrightarrow A_1B$
  - $A_1B + A_2 \Longrightarrow C$
- These processes are termed **reaction mechanisms**
  - Provide information regarding the order in which bonds are broken and formed
- Reaction mechanisms can be broken into elementary steps
  - The single steps that add up to the complete reaction mechanism
  - Described by the number of molecules acting as reactants
    - Molecularity
      - Unimolecular - one molecule breaking apart or rearranging
      - Bimolecular - involves the collision of two molecules
      - Termolecular - involves the collision of three molecules
        - Not very likely - rarely occur
      - More than three aren't generally used because they are so nonprobable
- These elementary steps are then added together to create a complete reaction mechanism

Reaction Mechanisms

Reaction Mechanisms and Molecularity

- Elementary steps are simple, <u>one step</u> reaction processes that depend only on the concentration of the reactants.
- The sum of these elementary steps is the complete mechanism for the reaction.
- Elementary steps are described by the number of particles actings as reactants
  - Unimolecular - one particle breaking apart or rearranging
  - Bimolecular - involves the collision of two particles
  - Termolecular - involves the collision of three particles
    - Not very likely - rarely occur
    - More than three aren't generally used because they are so improbable
- <u>Intermediates</u> are substances that are formed by one elementary step, then consumed by the next. Therefore, they don't appear in the balanced equation.

Reaction Mechanisms

Mechanisms and Rate Laws

- We ***cannot*** write rate laws for chemical reactions from balanced equations.
  - Instead, we must have reaction data
  - Why?
- We ***can*** write rate laws for elementary steps without experimental data from the balanced equation
  - The coefficients for the balanced elementary step equation **are** the exponents for the reactions orders in the rate law
  - Why is this true?
    - The rate law of an elementary step is based directly on its **molecularity** because the rate of the reaction is dependent on simple, **concentration dependent** collisions

Reaction Mechanisms

Relating Reaction Rate with Mechanisms

- For reactions that occur in multiple steps, the rate of the overall reaction cannot exceed the rate of the slowest elementary step.
- This slowest step is termed the **rate-determining step**
  - The reaction step that limits the overall rate of the reaction

Reaction Mechanisms

Verifying Rate Mechanisms

- The reaction between nitrogen dioxide and carbon monoxide, as represented below, is suggested to take place through the following 2 step mechanism. Verify that this mechanism is valid for this reaction.

$$NO_2 + CO \Rightarrow NO + CO_2$$

Step 1: $NO_2 + NO_2 \Rightarrow NO_3 + NO$

Step 2: $NO_3 + CO \Rightarrow NO_2 + CO_2$

Reaction Mechanisms

Verifying Rate Mechanisms

Trial #	$[NO_2]$	[CO]	Initial Rate
1	0.100	0.100	1.2×10^{-3}
2	0.100	0.200	1.2×10^{-3}
3	0.200	0.100	4.8×10^{-3}

Reaction Mechanisms

Verifying Rate Mechanisms

- The reaction between nitrogen dioxide and carbon monoxide, as represented below, is suggested to take place through the following 2 step mechanism. Verify that this mechanism is possible for this reaction.

$$NO_2 + CO \Rightarrow NO + CO_2$$

Slow Step 1: $NO_2 + NO_2 \Rightarrow NO_3 + NO$

Fast Step 2: $NO_3 + CO \Rightarrow NO_2 + CO_2$

Reaction Mechanisms

Homework

- 14.65 / 14.66 / 14.67 / 14.71 / 14.74
- Princeton Review
  - Free Response 1 & 2