Section 12.6
Reaction Mechanism

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Learning Objectives

- Distinguish net reactions from elementary reactions (steps)
- Identify the molecularity of elementary reactions
- Write a balanced chemical equation for a process given its reaction mechanism
- Derive the rate law consistent with a given reaction mechanism

Reaction Mechanisms

- Reactions often involve two or more distinct reactions taking place in sequence.
- The **reaction mechanism** (or reaction path) provides details regarding the precise, step-by-step process by which a reaction occurs.
- Each of the steps in a reaction mechanism is an **elementary reaction**.

Considering Elementary Reactions

- Elementary reactions are explicit representations of the chemical change taking place.
- They depict only the bond-breaking and/or making events depicted to yield the product(s).
- The rate law for an elementary reaction may be derived directly.
- This is not the case for typical chemical reactions, for which rate laws may be reliably determined only via experimentation.

Elementary Reactions

- The decomposition of ozone has two elementary steps.

$$O_3(g) \longrightarrow O_2(g) + O$$

$$O + O_3(g) \longrightarrow 2O_2(g)$$

- They sum to yield the overall equation for this reaction.

$$2O_3(g) \longrightarrow 3O_2(g)$$

- The oxygen atom produced in the first step of this mechanism is consumed in the second step. Species that are produced in one step and consumed in a subsequent step are called **intermediates**.

Unimolecular Elementary Reactions

- The **molecularity** of an elementary reaction is the number of reactant entities (atoms, molecules, or ions).
- A **unimolecular reaction** involves the reaction of a single reactant entities to produce one or more molecules of product:

$$A \longrightarrow \text{products}$$

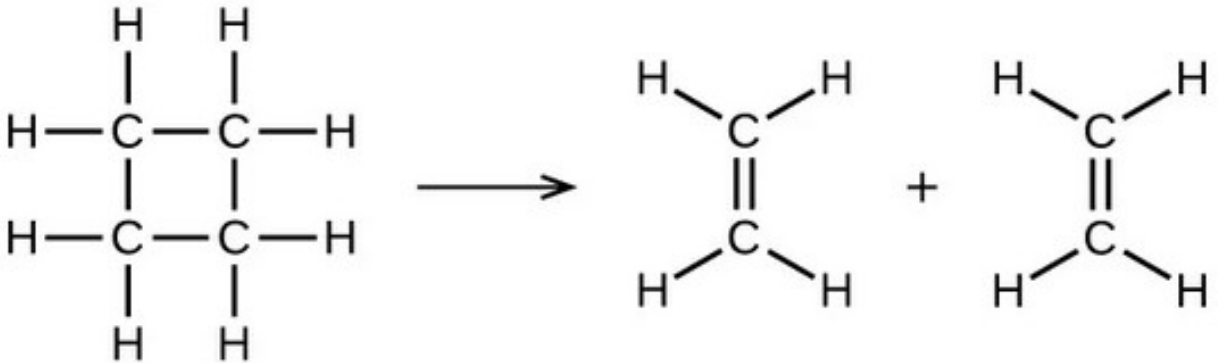
- The rate law for a unimolecular reaction is first order:

$$\text{rate} = k[A]$$

- A Unimolecular equation can be an elementary equation or an overall equation.

Unimolecular Equation Example

- The gas-phase decomposition of cyclobutane, C_4H_8, to ethylene, C_2H_4, is an example of a unimolecular equation that is both an elementary and overall equation:



$$\text{rate} = -\frac{\Delta[C_4H_8]}{\Delta t} = k[C_4H_8]$$

Bimolecular Elementary Reactions

- A **bimolecular reaction** involves two reactant entities:

$$A + B \longrightarrow \text{products} \qquad \text{rate} = k[A][B]$$

$$2A \longrightarrow \text{products} \qquad \text{rate} = k[A][A] = k[A]^2$$

- Some chemical reactions occur by mechanisms that consist of a single bimolecular elementary reaction.

$$\mathrm{NO_2}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{CO_2}(g)$$

$$\text{rate} = k\,[\mathrm{NO_2}][\mathrm{CO}]$$

Termolecular Elementary Reactions

- Although very rare there are some documented termolecular reactions involving the simultaneous collision of three molecules.

$$2\mathrm{NO} + \mathrm{O_2} \longrightarrow 2\mathrm{NO_2}$$

$$\text{rate} = k[\mathrm{NO}]^2[\mathrm{O_2}]$$

The Slowest Step

- It's often the case that one step in a multistep reaction mechanism is significantly slower than the others.
- The slowest step is called the **rate-limiting step** (or rate-determining step) of the reaction.
- The rate of the overall reaction will be determined by the slowest step.

$$\mathrm{NO_2}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{NO_3}(g) + \mathrm{NO}(g) \ \text{(slow)}$$

$$\mathrm{NO_3}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{NO_2}(g) + \mathrm{CO_2}(g) \ \text{(fast)}$$

$$\text{rate} = k[\mathrm{NO_2}]^2$$