Chapter 29

Reaction Mechanisms

29.1 TST and Overview of Mechanisms

4/18:

- Overview of key concepts.
  - Reaction mechanisms can involve more than one elementary step.
  - Reactions can be sequential (single- or multi-step).
  - To establish a mechanism, we use several techniques, approaches, assumptions, and approximations.
  - Establish rate determining steps: The rate law and rate constants associated with these steps tend to dominate the kinetics of the overall reaction.
  - Invoke the steady-state approximation to help solve the complicated mathematics of reaction kinetics.
  - Enzyme kinetics, Michaelis-Menten mechanism involves an SS approximation.
- Oftentimes, reactions are of the form

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \xrightarrow{k_r} \mathrm{P} + \mathrm{E}$$

  - Note that this form is very much analogous to the form analyzed in TST.
- **Elementary reaction**: A reaction that does not involve the formation of a reaction intermediate; the products must be formed directly from the reactants.
  - Denoted by the double arrow.
  - An elementary reaction can still be reversible.
- **Molecularity** (of an elementary reaction): The number of reactant molecules involved in the chemical reaction.
- **Unimolecular** (reaction): An elementary reaction with molecularity one. *General form*

$$\mathrm{A} \Longrightarrow \text{products}$$

  Rate law

$$v = k[\mathrm{A}]$$

- **Bimolecular** (reaction): An elementary reaction with molecularity two. *General form*

$$\mathrm{A} + \mathrm{B} \Longrightarrow \text{products}$$

  Rate law

$$v = k[\mathrm{A}][\mathrm{B}]$$

- **Termolecular** (reaction): An elementary reaction with molecularity three. *General form*

$$\mathrm{A} + \mathrm{B} + \mathrm{C} \Longrightarrow \text{products}$$

  Rate law

$$v = k[\mathrm{A}][\mathrm{B}][\mathrm{C}]$$

- No elementary reaction with molecularity greater than three is known, and the overwhelming majority of elementary reactions are bimolecular.
- When a complex reaction is at equilibrium, the rate of the forward process is equal to the rate of the reverse process for each and every step of the reaction mechanism.
  - We denote a reversible elementary reaction as follows.

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} + \mathrm{D}$$

  - A reversible elementary reaction signifies that the reaction occurs in both the forward and reverse directions to a significant extent and that the reaction in each direction is an elementary reaction.
  - The rate laws are

$$v_1 = k_1[\mathrm{A}][\mathrm{B}] \qquad\qquad v_{-1} = k_{-1}[\mathrm{C}][\mathrm{D}]$$

  - At equilibrium,

$$\begin{aligned} k_1[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}} &= k_{-1}[\mathrm{C}]_{\mathrm{eq}}[\mathrm{D}]_{\mathrm{eq}} \\ \frac{k_1}{k_{-1}} &= \frac{[\mathrm{C}]_{\mathrm{eq}}[\mathrm{D}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}}} = K_c \end{aligned}$$

- **Principle of detailed balance**: The following relationship, which holds for all reversible elementary reactions. *Given by*

$$K_c = \frac{k_1}{k_{-1}}$$