

# Chapter 29

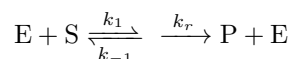
## Reaction Mechanisms

### 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.

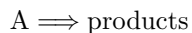
- Oftentimes, reactions are of the form



- 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.

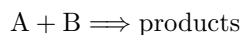
- **Unimolecular** (reaction): An elementary reaction with molecularity one. *General form*



*Rate law*

$$v = k[A]$$

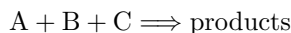
- **Bimolecular** (reaction): An elementary reaction with molecularity two. *General form*



*Rate law*

$$v = k[A][B]$$

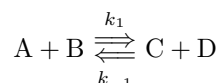
- **Termolecular** (reaction): An elementary reaction with molecularity three. *General form*



*Rate law*

$$v = k[A][B][C]$$

- 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.



- 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

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

- At equilibrium,

$$k_1[A]_{\text{eq}}[B]_{\text{eq}} = k_{-1}[C]_{\text{eq}}[D]_{\text{eq}}$$

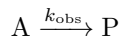
$$\frac{k_1}{k_{-1}} = \frac{[C]_{\text{eq}}[D]_{\text{eq}}}{[A]_{\text{eq}}[B]_{\text{eq}}} = K_c$$

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

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

## 29.2 The Two-Step Consecutive Reaction Mechanism

- 4/20:
  - Consider the general complex reaction



- Suppose that the reaction occurs by the two step mechanism



- Because each step of this mechanism is an elementary reaction, the rate laws for each species are

$$\frac{d[A]}{dt} = -k_1[A] \qquad \frac{d[I]}{dt} = k_1[A] - k_2[I] \qquad \frac{d[P]}{dt} = k_2[I]$$

- Thus, assuming that the initial concentrations at time  $t = 0$  are  $[A] = [A]_0$  and  $[I]_0 = [P]_0 = 0$ , we have that

$$[A] = [A]_0 e^{-k_1 t}$$

$$[I] = \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$[P] = [A]_0 - [A] - [I] = [A]_0 \left\{ 1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right\}$$

- Distinguishing the two-step consecutive reaction mechanism unambiguously from the one-step reaction.

- For a single step reaction,

$$[P] = [A]_0(1 - e^{-k_1 t})$$

- The two-step consecutive reaction mechanism has the following alternate form.

$$[P] = [A]_0 \left\{ 1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right\}$$

- However, if  $k_2 \gg k_1$ , then

$$\begin{aligned} [P] &= [A]_0 \left\{ 1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right\} \\ &\approx [A]_0 \left\{ 1 + \frac{1}{-k_2} k_2 e^{-k_1 t} \right\} \\ &= [A]_0(1 - e^{-k_1 t}) \end{aligned}$$

- If  $k_1 \gg k_2$ , the reaction reduces to

$$[P] \approx [A]_0(1 - e^{-k_2 t})$$

- Thus, the only ambiguous situation is  $k_2 \gg k_1$ .

- The steady-state approximation simplifies rate expressions.

- We assume that  $d[I]/dt = 0$ , where I is a reaction intermediate.

- Given the above differential equation for  $d[I]/dt$ , making the above assumption yields

$$[I]_{ss} = \frac{k_1[A]}{k_2}$$

- It follows that

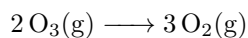
$$[I]_{ss} = \frac{k_1}{k_2} [A]_0 e^{-k_1 t}$$

- Thus,

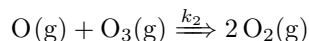
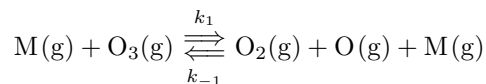
$$\frac{d[I]_{ss}}{dt} = \frac{-k_1^2}{k_2} [A]_0 e^{-k_1 t}$$

- We get  $k_2 \gg k_1^2[A]_0$  and  $[P] = [A]_0(1 - e^{-k_1 t})$ .

- Example: Decomposition of ozone.



- The reaction mechanism is



where M is a molecule that can exchange energy with the reacting ozone molecule through a collision, but M itself does not react.

- The rate equations for  $\text{O}_3(\text{g})$  and  $\text{O}(\text{g})$  are

$$\begin{aligned} \frac{d[\text{O}_3]}{dt} &= -k_1[\text{O}_3][\text{M}] + k_{-1}[\text{O}_2][\text{O}][\text{M}] - k_2[\text{O}][\text{O}_3] \\ \frac{d[\text{O}]}{dt} &= k_1[\text{O}_3][\text{M}] - k_{-1}[\text{O}_2][\text{O}][\text{M}] - k_2[\text{O}][\text{O}_3] \end{aligned}$$

- Invoking the steady-state approximation for the intermediate O yields

$$[\text{O}] = \frac{k_1[\text{O}_3][\text{M}]}{k_{-1}[\text{O}_2][\text{M}] + k_2[\text{O}_3]}$$

- Substituting this result into the rate equation for  $\text{O}_3$  gives

$$\frac{d[\text{O}_3]}{dt} = -\frac{2k_1k_2[\text{O}_3]^2[\text{M}]}{k_{-1}[\text{O}_2][\text{M}] + k_2[\text{O}_3]}$$