

Chapter 29

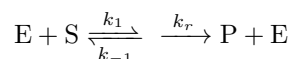
Reaction Mechanisms

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.

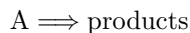
- Oftentimes, reactions are of the form



- 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.

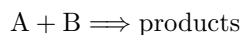
- **Unimolecular** (reaction): An elementary reaction with molecularity one. *General form*



Rate law

$$v = k[A]$$

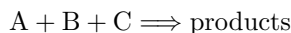
- **Bimolecular** (reaction): An elementary reaction with molecularity two. *General form*



Rate law

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

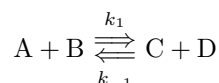
- **Termolecular** (reaction): An elementary reaction with molecularity three. *General form*



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,

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

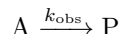
$$\frac{k_1}{k_{-1}} = \frac{[C]_{\text{eq}}[D]_{\text{eq}}}{[A]_{\text{eq}}[B]_{\text{eq}}} = K_c$$

- **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

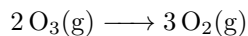
$$[I]_{ss} = \frac{k_1}{k_2} [A]_0 e^{-k_1 t}$$

- Thus,

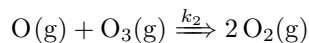
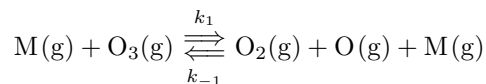
$$\frac{d[I]_{ss}}{dt} = \frac{-k_1^2}{k_2} [A]_0 e^{-k_1 t}$$

- 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

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

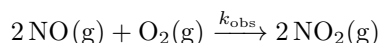
- Substituting this result into the rate equation for O_3 gives

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

29.3 Complex Reactions

- 4/22:
- Expect the midterm to be 2 hours in length, available all next week, and to incorporate largely HW-like questions but also some open-ended, design-an-experiment questions. Completely open note.
 - The rate law for a complex reaction does not imply a unique mechanism.

- Consider the reaction

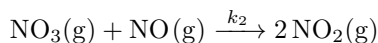
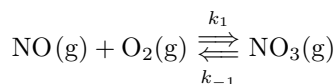


- The rate law is

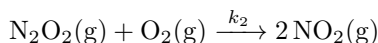
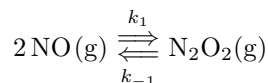
$$\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_{\text{obs}}[\text{NO}]^2[\text{O}_2]$$

- Experimental studies confirm that the reaction is not an elementary reaction, but we can propose multiple mechanisms that would both yield the same rate law. Here are two examples.

■ Mechanism 1.

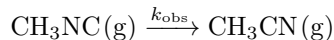


■ Mechanism 2.



- One experiment to design is to capture or otherwise detect the intermediate species.
- Through such an experiment, we can verify Mechanism 2.
- The Lindemann Mechanism explains how unimolecular reactions occur.

- Consider the reaction



- The following rate law is only correct at $[\text{CH}_3\text{NC}]$.

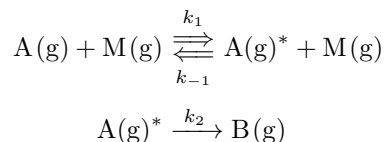
$$\frac{d[\text{CH}_3\text{NC}]}{dt} = -k_{\text{obs}}[\text{CH}_3\text{NC}]$$

- At low $[\text{CH}_3\text{NC}]$, we have

$$\frac{d[\text{CH}_3\text{NC}]}{dt} = -k_{\text{obs}}[\text{CH}_3\text{NC}]^2$$

which is not the rate law for a unimolecular reaction.

- The Lindemann mechanism for unimolecular reactions of the form $A(g) \longrightarrow B(g)$ is



- The symbol $A(g)^*$ represents an energized reactant molecule. $M(g)$ is the collision partner.
- By the steady-state approximation, we have that

$$\frac{d[A^*]}{dt} = 0 = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*]$$

$$[A^*] = \frac{k_1[M][A]}{k_2 + k_{-1}[M]}$$

so that

$$\frac{d[B]}{dt} = k_2[A^*]$$

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = \underbrace{\frac{k_2 k_1 [M]}{k_2 + k_{-1} [M]}}_{k_{\text{obs}}} [A]$$

- At high $[M]$, we have that $k_{-1}[M][A^*] \gg k_2[A^*]$, or $k_{-1}[M] \gg k_2$. Thus,

$$k_{\text{obs}} = \frac{k_1 k_2}{k_{-1}}$$

- At low $[M]$, we have that $k_2 \gg k_{-1}[M]$ so that

$$\frac{d[B]}{dt} = k_1[M][A]$$

$$= k_1[A]^2$$

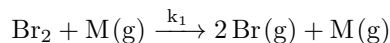
- This mechanism was proposed by the British chemists J. A. Christiansen in 1921 and F. A. Lindemann in 1922. Their work underlies the current theory of unimolecular reaction rates.

- Some reaction mechanisms involve chain reactions.

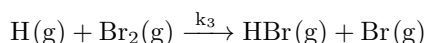
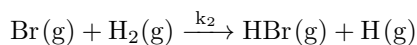
- Chain reactions involve amplification.

- For example, $H_2(g) + Br_2(g) \rightleftharpoons 2 HBr(g)$ follows the ensuing mechanism.

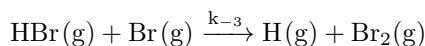
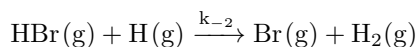
■ Initiation.



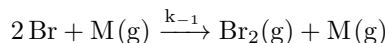
■ Propagation.



■ Inhibition.



■ Termination.



- The fifth step can be ignored.
- Notice that the inhibition and termination reactions are the reverse reactions of the propagation and initiation reaction(s), respectively.
 - Termination does not need to be the reverse of initiation, though. Termination just kills any reactive species.
 - Inhibition is the reverse of propagation, though.
- When you want to design a chain reaction species, make sure you have a reactive species (like bromine) for the initiation step. Notice, for instance, that hydrogen does not initiate.
- This leads to the experimentally determined rate law

$$\frac{1}{2} \frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k'[\text{HBr}][\text{Br}_2]^{-1}}$$

- Deriving said rate law.

■ We have that

$$\begin{aligned} \frac{d[\text{HBr}]}{dt} &= k_2[\text{Br}][\text{H}_2] - k_{-2}[\text{HBr}][\text{H}] + k_3[\text{H}][\text{Br}_2] \\ \frac{d[\text{H}]}{dt} &= k_2[\text{Br}][\text{H}_2] - k_{-2}[\text{HBr}][\text{H}] - k_3[\text{H}][\text{Br}_2] \\ \frac{d[\text{Br}]}{dt} &= 2k_1[\text{Br}_2][\text{M}] - k_{-1}[\text{Br}]^2[\text{M}] - k_2[\text{Br}][\text{H}_2] + k_{-2}[\text{HBr}][\text{H}] + k_3[\text{H}][\text{Br}_2] \end{aligned}$$

- We can apply the SS approximation to the second and third equations above, which both describe intermediate species.

$$\begin{aligned} 0 &= k_2[\text{Br}][\text{H}_2] - k_{-2}[\text{HBr}][\text{H}] - k_3[\text{H}][\text{Br}_2] \\ 0 &= 2k_1[\text{Br}_2][\text{M}] - k_{-1}[\text{Br}]^2[\text{M}] - k_2[\text{Br}][\text{H}_2] + k_{-2}[\text{HBr}][\text{H}] + k_3[\text{H}][\text{Br}_2] \end{aligned}$$

- Solving the two equations above for [H] and [Br], respectively, is made substantially easier by noting that the negative of the first expression appears in its entirety in the second expression. Thus, we may simply substitute the former into the latter and solve to find an expression for [Br].

$$\begin{aligned} 0 &= 2k_1[\text{Br}_2][\text{M}] - k_{-1}[\text{Br}]^2[\text{M}] - 0 \\ [\text{Br}] &= \left(\frac{k_1}{k_{-1}} \right)^{1/2} [\text{Br}_2]^{1/2} \\ [\text{Br}] &= (K_{c,1})^{1/2} [\text{Br}_2]^{1/2} \end{aligned}$$

- Resubstituting yields an expression for [H].

$$\begin{aligned} 0 &= k_2[\text{Br}][\text{H}_2] - k_{-2}[\text{HBr}][\text{H}] - k_3[\text{H}][\text{Br}_2] \\ 0 &= k_2(K_{c,1})^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2] - (k_{-2}[\text{HBr}] + k_3[\text{Br}_2])[H] \\ [\text{H}] &= \frac{k_2(K_{c,1})^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} \end{aligned}$$

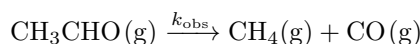
- Substituting these two expressions back into the original differential equation for [HBr] yields

$$\begin{aligned}
 \frac{d[\text{HBr}]}{dt} &= k_2[\text{Br}][\text{H}_2] - k_{-2}[\text{HBr}][\text{H}] + k_3[\text{H}][\text{Br}_2] \\
 &= k_2(K_{c,1})^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2] - k_{-2}[\text{HBr}] \cdot \frac{k_2(K_{c,1})^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} \\
 &\quad + k_3 \cdot \frac{k_2(K_{c,1})^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} \cdot [\text{Br}_2] \\
 &= k_2(K_{c,1})^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2] - \frac{k_2 k_{-2}(K_{c,1})^{1/2}[\text{HBr}][\text{Br}_2]^{1/2}[\text{H}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} \\
 &\quad + \frac{k_2 k_3(K_{c,1})^{1/2}[\text{Br}_2]^{3/2}[\text{H}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} \\
 &= k_2(K_{c,1})^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2] \left(1 - \frac{k_{-2}[\text{HBr}]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} + \frac{k_3[\text{Br}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} \right) \\
 &= k_2(K_{c,1})^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2] \left(\frac{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} - \frac{k_{-2}[\text{HBr}] - k_3[\text{Br}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} \right) \\
 &= k_2(K_{c,1})^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2] \cdot \frac{2k_3[\text{Br}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} \\
 \frac{1}{2} \frac{d[\text{HBr}]}{dt} &= k_2(K_{c,1})^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2] \cdot \frac{1}{(k_{-2}/k_3)[\text{HBr}][\text{Br}_2]^{-1} + 1} \\
 &= \frac{k_2(K_{c,1})^{1/2}[\text{H}_2][\text{Br}_2]^{1/2}}{1 + (k_{-2}/k_3)[\text{HBr}][\text{Br}_2]^{-1}} \\
 &= \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k'[\text{HBr}][\text{Br}_2]^{-1}}
 \end{aligned}$$

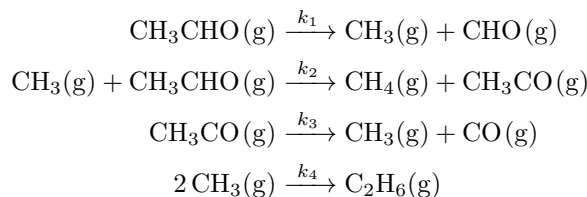
where we have substituted $k = k_2(K_{c,1})^{1/2}$ and $k' = k_{-2}/k_3$ in the last expression.

• Problem 29-24.

- The reaction



proceeds by the mechanism



- The initiation step is the first equation, the propagation steps are the second and third equations, and the termination step is the fourth equation.
- We can write the rate laws

$$\begin{aligned}
 \frac{d[\text{CH}_4]}{dt} &= k_2[\text{CH}_3][\text{CH}_3\text{CHO}] \\
 \frac{d[\text{CH}_3]}{dt} &= k_1[\text{CH}_3\text{CHO}] - k_2[\text{CH}_3][\text{CH}_3\text{CHO}] + k_3[\text{CH}_3\text{CO}] - 2k_4[\text{CH}_3] \\
 \frac{d[\text{CH}_3\text{CO}]}{dt} &= k_2[\text{CH}_3][\text{CH}_3\text{CHO}] - k_3[\text{CH}_3\text{CO}]
 \end{aligned}$$

- Applying the SS approximation to the last second and third equations yields (respectively)

$$[\text{CH}_3] = \frac{k_1[\text{CH}_3\text{CHO}] + k_3[\text{CH}_3\text{CO}]}{k_2[\text{CH}_3\text{CHO}] + 2k_4} \qquad [\text{CH}_3\text{CO}] = \frac{k_2}{k_3}[\text{CH}_3][\text{CH}_3\text{CHO}]$$

- Substituting the right equation above into the left equation above and solving for $[\text{CH}_3]$ yields an expression for $[\text{CH}_3]$ purely in terms of $[\text{CH}_3\text{CHO}]$.

$$\begin{aligned} [\text{CH}_3] &= \frac{k_1[\text{CH}_3\text{CHO}] + k_2[\text{CH}_3][\text{CH}_3\text{CHO}]}{k_2[\text{CH}_3\text{CHO}] + 2k_4} \\ k_2[\text{CH}_3][\text{CH}_3\text{CHO}] + 2k_4[\text{CH}_3] &= k_1[\text{CH}_3\text{CHO}] + k_2[\text{CH}_3][\text{CH}_3\text{CHO}] \\ 2k_4[\text{CH}_3] &= k_1[\text{CH}_3\text{CHO}] \\ [\text{CH}_3] &= \frac{k_1}{2k_4}[\text{CH}_3\text{CHO}] \end{aligned}$$

- The final result is

$$\begin{aligned} \frac{d[\text{CH}_4]}{dt} &= k_2 \left(\frac{k_1}{2k_4}[\text{CH}_3\text{CHO}] \right) [\text{CH}_3\text{CHO}] \\ &= k_2 \left(\frac{k_1}{2k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2} \end{aligned}$$

■ What's the issue here?