

Chapter 29

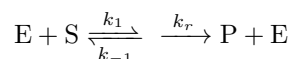
Reaction Mechanisms

29.1 TST and Overview of Mechanisms

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- 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.

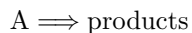
- Oftentimes, reactions are of the form



- 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.

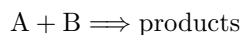
- **Unimolecular** (reaction): An elementary reaction with molecularity one. *General form*



Rate law

$$v = k[A]$$

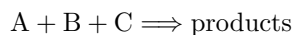
- **Bimolecular** (reaction): An elementary reaction with molecularity two. *General form*



Rate law

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

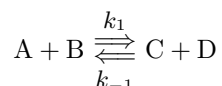
- **Termolecular** (reaction): An elementary reaction with molecularity three. *General form*



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

$$v_1 = k_1[A][B]$$

$$v_{-1} = k_{-1}[C][D]$$

- 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*

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