

CHEM 3410: Physical Chemistry I — Fall 2008

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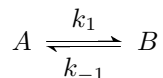
Lecture 32: More on reaction mechanisms & steady state

References

1. Levine, *Physical Chemistry*, Chapter 16

Key Concepts

- In consecutive or series reactions, a reactant, A forms an intermediate B, which then forms the product C.
 - The solution for $[A](t)$ was arrived at using the first order kinetics we discussed previously. The rate at which $[A]$ decreases depends on the rate constant of the $A \rightarrow B$ reaction, k_1 .
 - The time dependence of $[B]$ can be obtained by solving a differential equation similar to the case for parallel reactions. $[C]$ can be found by evoking mass conservation.
 - The rate limiting step will determine the observed concentration behavior for A, B, and C. It is determined by the relative values of k_1 and k_2 .
- In a reversible reaction, we can arrive at a relationship between rate constants and the equilibrium constant. Consider:



where

$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}}$$

At equilibrium, the rates of the forward and reverse reactions are equal, leading to:

$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_1}{k_{-1}}$$

- For the reaction mechanisms discussed so far, we had to solve some differential equations to determine the concentration of each species as a function of time. We can simplify this process by evoking the steady-state approximation.
- We can only do this if we can safely assume that the concentration of intermediates is small and constant with time. For a mechanism with a single intermediate, B, the assumption is that:

$$\frac{d[B]}{dt} \approx 0$$

- The steady state approximation (the concentration of an intermediate is constant or time independent) allows us to:
 1. remove intermediate concentrations from rate expressions for reactants or products of the overall reaction. This allows us to arrive at rate expressions that can be compared to experimental data
 2. solve algebraic equations as opposed to differential equations
- The steady state approximation is valid in cases where intermediates form slowly but are used up quickly.