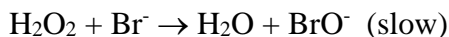# CHAPTER 11
ACCOUNTING FOR THE RATE LAWS
CHAPTER OUTLINE

HW: Questions are below. Solutions are in separate file on the course web site.

Sect.	Material

1.   Reaction Mechanisms

2.   The Steady-State Approximation

3.   Introduction to Enzyme Kinetics

4.   The Michaelis-Menten Mechanism

5.   Determination of Michaelis-Menten Parameters

6.   Enzyme Inhibition

7.   Competitive Inhibition

8.   Uncompetitive Inhibition

9.   Noncompetitive Inhibition

10.   Enzyme Inhibition: Summary

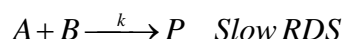11.   Quantitative Aspects of Enzyme Inhibition

Chapter 11 Homework

11.1 The reaction $2 H_2O_2(aq) \rightarrow 2 H_2O(l) + O_2(g)$ is catalyzed by Br^- ions. If the mechanism is:

$$H_2O_2 + Br^- \rightarrow H_2O + BrO^-\ \text{(slow)}$$

$$BrO^- + H_2O_2 \rightarrow H_2O + O_2 + Br^-\ \text{(fast)}$$

Give the predicted rate law.

11.2 The reaction mechanism involves an intermediate, A. The mechanism is

$$A_2 \xleftrightarrow{K} A + A\ \textit{Fast Equilibrium}$$

$$A + B \xrightarrow{k} P\ \textit{Slow RDS}$$

What is the rate law for the formation of P?

11.3 The reaction, $2A + B \rightarrow P$ (P is the product), proceeds via a rapid pre-equilibrium (with equilibrium constant, K) followed by a slow rate determining step (with rate constant, k_2) as shown below:

$$2A \overset{K}{=} A_2\ \text{(fast pre-equilbrium)}$$

$$A_2 + B \overset{k_2}{\rightarrow} \text{Products}\ \text{(slow)}$$
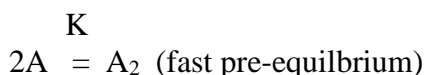
Develop an expression for the rate of formation of Products as a function of [A], [B], K and k_2.

11.4 The following mechanism has been proposed for the decomposition of ozone in the atmosphere.

$$O_3 \underset{k_{-1}}{\overset{k_1}{=}} O_2 + O$$

$$O + O_3 \overset{k_2}{\rightarrow} O_2 + O_2$$
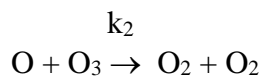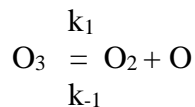
Use the steady-state approximation on [O] to develop an expression for the rate of the reaction, $-d[O_3]/dt$.

Show that if the k_2 step is slow, then the rate is second-order in $[O_3]$ and of order -1 in $[O_2]$.

11.5 The condensation reaction of acetone (HA) in aqueous solution is catalyzed by a base (B), that reacts reversibly with acetone to form the carbanion (A^-). The carbanion then reacts with an acetone to form the product. The Mechanism is:

$$AH + B \xrightarrow{k_1} BH^+ + A^- \quad Formation\ of\ Carbanion$$

$$A^- + BH^+ \xrightarrow{k_2} AH + B \quad Re\,verse\ of\ reaction\,1$$

$$A^- + AH \xrightarrow{k_3} Pr\,oduct \quad Re\,action\ to\ form\ product$$
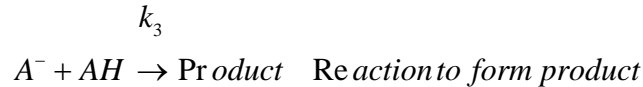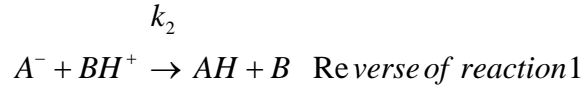
Use the steady-state approximation on the intermediate, [A^-], to derive the rate equation for the formation of product.

11.6 The reaction, $A + B + C \rightarrow P$ (P is the product) proceeds by the following mechanism.

$$A + B \underset{k_{-1}}{\overset{k_1}{=}} I$$

$$I + C \xrightarrow{k_2} P$$
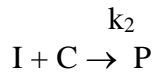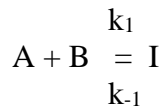
"I" is an intermediate present in steady-state concentration. Use the steady-state approximation on [I] to develop an expression for the rate of formation of P as a function of [A], [B], [C], k_1, k_{-1} and k_2.

11.7 Analyze of the enzyme-catalyzed conversion of a substrate to form product at 25 $^\circ$C yields a Michaelis Constant of 0.045 mol/L.

The rate of the reaction is 1.15 mM/s (milliMolar/s) when the substrate concentration is 0.110 mol/L

What is the maximum velocity, V_m, for this reaction?

11.8 The hydrolysis of the substrate, N-glutaryl-L-phenylalanine-p-nitroanilide [GPNA], to p-nitroaniline and N-glutaryl-L-phenylanine is catalyzed by α-chymotrypsin. When $[E]_o = 4.0 \times 10^{-6}$ M, it is found that $v_o = 3.7 \times 10^{-8}$ M/s when $[S] = 2.5 \times 10^{-4}$ M and $v_o = 9.8 \times 10^{-8}$ M/s when $[S] = 1.0 \times 10^{-3}$ M.

Determine the slope and intercept of the Lineweaver-Burk plot and, from these, K_M, V_m, and k_2 for this reaction.

11.9 An enzyme has the Michaelis-Menten parameters, $K_M = 2.8 \times 10^{-5}$ M and $V_m = 53$ µM/min. For $[S] = 7.5 \times 10^{-5}$ M and $[I] = 4.8 \times 10^{-4}$ M, and $K_I = 1.7 \times 10^{-4}$ M, calculate the initial rate $[(v_o)_{inh}]$ and the percent inhibition $[i\%]$ for (a) competitive inhibition, (b) uncompetitive inhibition, and (c) nonncompetitive inhibition.

11.10 An enzyme-catalyzed reaction with $K_M = 2.7 \times 10^{-3}$ M is inhibited by a competitive inhibitor ($K_I = 3.1 \times 10^{-5}$ M). When the substrate concentration is 3.6×10^{-4} M, what inhibitor concentration, $[I]$, is required to get 65% inhibition.

11.11 For an enzyme-catalyzed reaction, v_o was measured as a function of $[S]$, and the Lineweaver-Burk plot ($1/v_o$ vs. $1/[S]$) below was obtained.

Analysis of the graph shows that the Slope = 0.0133 s and Intercept = 0.0334 s/mM

Note: Determination of the slope and intercept is given in the solution. However, you will not be asked to perform the graphical analysis on a test.

Determine the maximum velocity, Vm, and the Michaelis Constant, K_M, for this reaction.