Handin 4: Kinetics Mechanisms

1. The decomposition of superoxide in surface waters is given by the reaction:

$$4 \; HO_2 \rightarrow H_2O_2 + HO_2^- + H^+ + 2 \; O_2$$

This reaction is one of the steps in the photochemical redox cycling of Fe(II) and Fe(III) in lakes and rivers. The proposed mechanism is:

$$HO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H^+ + O_2^-$$

$$2 \; HO_2 \overset{k_2}{\rightarrow} H_2O_2 + O_2$$

$$HO_2 + O_2^- \overset{k_3}{\rightarrow} HO_2^- + O_2$$
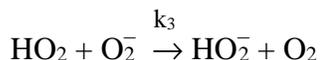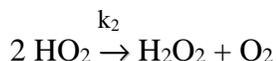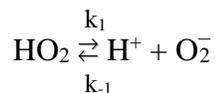
Use the steady-state approximation to show the rate law for this mechanism is in the form:

$$\frac{d[O_2]}{dt} = k_{eff} \; [HO_2]^2$$

The HO_2 concentration in natural waters is very low, sub nano-molar; $[HO_2] < 1 \times 10^{-9}$ M. Proton transfer reactions are some of the fastest reactions known, so k_{-1} is large, $\sim 10^{15}$. Assume an acidic process so $k_{-1}[H^+]$ is large and approximately constant (HO_2 is the limiting reagent). [Try Chapter 4 Problems 8 and 10 first]

2. Using the Principle of Detailed Balance, show that the mechanism in Problem 1 generates the expected overall equilibrium ratio when the reaction is at equilibrium:

$$K_{eq} = \left(\frac{[H_2O_2][\; HO_2^-][H^+][O_2]^2}{[HO_2]^4} \right)_{eq}$$

Assume that the reverse rate constants are given as k_{-1}, k_{-2}, k_{-3}. Give the relationship between the rate constants and the equilibrium constant. [Try Chapter 4 Problem 29 first]

3. The reaction $A + C \rightleftarrows D$ is proposed to have the following mechanism:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

$$B + C \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} D$$
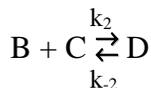
(a). Show that near equilibrium: $\qquad \dfrac{d[A]}{dt} = - k_1 \; [A] + k_{-1} \; \dfrac{k_1[A] + k_{-2}[D]}{k_{-1} + k_2[C]}$

(b). In terms of the <u>overall</u> process, $A + C \rightleftarrows D$, <u>near equilibrium</u> but not necessarily at equilibrium, we write the <u>overall</u> rate law in terms of the initial reactants and the final product as:

$$\upsilon = - \frac{d[A]}{dt} = k_f \; [A][C] - k_r \; [D]$$

Show that the equation in part (a) reduces to this last overall equation, assuming a rapid pre-equilibrium. From the equation that you derive, find the relationship between the overall equilibrium constant and the four rate constants for the mechanistic steps. [In other words, don't use detailed balance directly as you did in Problem 2, work from the rate law in part (a).]
[Try Chapter 4 Problems 30 and 31 first]