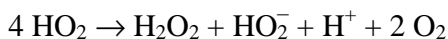
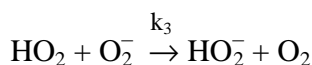
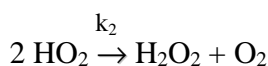
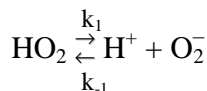


Handin 4: Kinetics Mechanisms

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



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:



Use the steady-state approximation to show the rate law for this mechanism is in the form:

$$\frac{d[\text{O}_2]}{dt} = k_{\text{eff}} [\text{HO}_2]^2$$

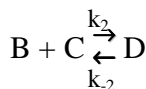
The HO_2 concentration in natural waters is very low, sub nano-molar; $[\text{HO}_2] < 1 \times 10^{-9}$ M. Proton transfer reactions are some of the fastest reactions known, so k_1 is large, $\sim 10^{15}$. Assume an acidic process so $k_{-1}[\text{H}^+]$ is large and approximately constant (HO_2 is the limiting reagent).

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:

$$K_{\text{eq}} = \left(\frac{[\text{H}_2\text{O}_2][\text{HO}_2^-][\text{H}^+][\text{O}_2]^2}{[\text{HO}_2]^4} \right)_{\text{eq}}$$

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.

3. The reaction $\text{A} + \text{C} \rightleftharpoons \text{D}$ is proposed to have the following mechanism:



(a). Show that near equilibrium: $\frac{d[\text{A}]}{dt} = -k_1 [\text{A}] + k_{-1} \frac{k_1[\text{A}] + k_{-2}[\text{D}]}{k_{-1} + k_2[\text{C}]}$

(b). In terms of the overall process, $\text{A} + \text{C} \rightleftharpoons \text{D}$, at equilibrium we write the overall rate law in terms of the initial reactants and the final product as:

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

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).]