## **Chemical Kinetics: Reaction Mechanisms II (covering Topic 4b)**

## Chemistry 126

1. The reaction of iron(II) and thallium(III) follows the overall equation

$$2\text{Fe}^{2+}(aq) + \text{Tl}^{3+}(aq) \rightarrow 2\text{Fe}^{3+}(aq) + \text{Tl}^{+}(aq)$$

Deduce the expected rate law for this chemical reaction based on the following mechanism. Assume that the first step is fast enough relative to the second to establish a pre-equilibrium situation.

$$\operatorname{Fe}^{2+}(aq) + \operatorname{Tl}^{3+}(aq) = \frac{k_1}{k_{-1}} \operatorname{Fe}^{3+}(aq) + \operatorname{Tl}^{2+}(aq)$$

$$\operatorname{Fe}^{2^{+}}(aq) + \operatorname{Tl}^{2^{+}}(aq) \xrightarrow{k_{2}} \operatorname{Fe}^{3^{+}}(aq) + \operatorname{Tl}^{+}(aq)$$

2. The DNA double helix contains two complementary single strands composed of adenine, thymine, guanine, and cytosine nucleotide bases. Hydrogen bonding between the bases of these complementary strands holds the double helix together. A mechanism proposed for the *renaturation* of the DNA double helix (the formation of the double helix from its two complementary strands A and B) is shown below. This mechanism supposes that the reaction proceeds via an unstable double helix that contains base pair misalignments between the single strands A and B. Determine the expected rate law for the renaturation of DNA based on this mechanism.

strand A + strand B 
$$\xrightarrow{k_1}$$
 unstable helix  $k_2$  unstable helix  $\rightarrow$  stable DNA double helix

3. Given the following mechanism (and assuming the pre-equilibrium approximation):

$$I_2 \qquad \underbrace{\qquad \qquad }_{k_{-1}} \qquad 2 I$$

$$H_2 + I = \frac{k_2}{k_{-2}} \qquad H_2I$$

$$k_3$$
 $H_2I + I \rightarrow 2 HI$ 

- (a) Identify the overall equation.
- (b) Identify any intermediates.
- (c) Determine the expected rate law for this reaction.
- (d) What is the concentration of  $I_2$  after 10 minutes starting from an initial concentration of 0.1 M if  $k_1/k_{-1} = 10^{-4}$ ,  $k_2/k_{-2} = 10^2$ ,  $k_3 = 0.1$  L mol<sup>-1</sup> min<sup>-1</sup>, and  $[H_2] = 3.0$  M. (Hint: Assume the concentration of  $I_2$  is constant. That is, form a pseudo-rate constant by combining the rate constants from the mechanistic steps and  $[I_2]$ .)