Chemistry 2710 Spring 2006 Test 2

Time: 50 minutes

Marks: 48

Aids allowed: Calculator, formula sheet

Instructions: Answer all questions in the booklets provided. You are expected to use your graphing calculator to draw graphs. A reasonable facsimile of your graph with properly labeled axes should be drawn in your exam booklet.

Useful data:

1. Sketch the apparatus used in the stopped-flow experiment and explain how it works, focusing particularly on aspects which make it suitable for the study of fast reactions. [10 marks]

2. The mechanism for the reaction

$$Hg^{2+}_{2(aq)} + Tl^{3+}_{(aq)} \rightarrow 2Hg^{2+}_{(aq)} + Tl^{+}_{(aq)}$$

is thought to be

$$Hg^{2+}_{2(aq)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Hg^{2+}_{(aq)} + Hg_{(aq)} \qquad \text{(fast)},$$

$$Hg_{(aq)} + Tl^{3+}_{(aq)} \overset{k_2}{\rightarrow} Hg^{2+}_{(aq)} + Tl^{+}_{(aq)} \quad \text{(slow)}.$$

   (a) What rate law would you predict based on this mechanism? [8 marks]

   (b) Suppose that we carried out two initial rate experiments where, all other factors being held constant, we doubled the concentration of the mercury (II) ion from one experiment to the next. What effect would this have on the rate? [2 marks]

3. The hydration of fumarate (F) catalyzed by the enzyme fumarase is inhibited by succinate (S).[1] The following data have been obtained for this reaction:[2]

$[\mathrm{F}]/10^{-4}\mathrm{mol\,L^{-1}}$	$v/\mathrm{u\,s^{-1}}$	
5.0	3.36	2.74
1.5	2.45	1.72
0.8	1.79	1.13
0.5	1.33	0.79
$[\mathrm{S}]/\mathrm{mol\,L^{-1}}$	0	0.05

Determine whether these data are consistent with competitive or uncompetitive inhibition, or neither. If the type is competitive or uncompetitive, determine the values of K_S (or K_E) and K_I. [20 marks]

4. Consider a living cell which is producing a substance X at a constant rate k_0 and degrading this substance in an enzyme-catalyzed reaction. A simplified rate equation describing this situation would be

$$\frac{dx}{dt} = k_0 - \frac{v_{\max} x}{x + K_M}.$$

(a) Show that there is a single equilibrium point provided k_0 is not too large. [4 marks]

Hints: Note that the Michaelis-Menten term in the rate equation has a maximum value. If you write down the equilibrium condition, you can turn the problem of finding the equilibrium point into one of finding an intersection between two curves (one of which is trivial). This will give you a pictorial proof.

(b) Using methods from nonlinear dynamics, show that this equilibrium point is always stable (provided it exists). In other words, show that a cell can maintain a stable level of X by balancing production with enzymatic degradation. [4 marks]

Important: For full marks in these questions you must explain your reasoning.

[1] **Important:** S is being used here to denote the inhibitor succinate *not* the substrate.

[2] In some enzyme experiments, we are only able to measure a signal which is proportional to the product concentration without knowing what the proportionality constant is. In these cases, the rate is given in arbitrary units (u) per second.