Chemistry 2710 Spring 2004 Test 3

Total marks: 48

Aids allowed: Calculator. One $8\frac{1}{2} \times 11$-inch piece of paper containing any information you need. No other printed materials (e.g. periodic tables, calculator manuals) are allowed.

Instructions: Answer all questions in the booklets provided.

Graphs should *either* be sketched in your exam booklet (if you are using a graphing calculator) or drawn on the graph paper provided. If you are hand-drawing graphs, make sure to put your name and the question number on the graph paper. If you decide to use a graphing calculator, provide a clearly labeled and reasonably accurate sketch of any graphs used in answering a question.

Clarity may be considered in evaluating your answers. Make sure to explain your reasoning (in a few words) for any mathematical derivation or calculation presented.

1. Suppose that the reaction $A + 2B \rightarrow P$ has an empirical rate law $v = kab$. The reactants A and B are pumped into a CSTR from separate reservoirs. The concentrations of A and B in the reservoirs are, respectively, a_i and b_i. With certain types of pumps, it is possible to arrange for the pumping rate from both reservoirs to be the same. Suppose that this is the case. Write down the rate equations for the concentrations of B and P in the CSTR. Clearly indicate the meanings of any symbols appearing in your rate equations which were not defined here. [6 marks]

2. Hammond et al. have studied the hydroxylation of estradiol by hamster kidney microsomes (a preparation which typically includes a number of enzymes, as well as their biochemical support systems).[1] The following data were obtained for hydroxylation at carbon-2:[2]

[estradiol] (μmol/L)	83.9	31.5	21.3	8.5	4.3	1.2
v (nmol g^{-1}min^{-1})	15.3	10.1	8.2	4.5	2.6	0.8

Do these data follow the Michaelis-Menten rate law? If so, determine $v_{\max}$ and K_M. If not, explain what feature(s) of the data led you to your conclusion. [8 marks]

[1] D. K. Hammond, B. T. Zhu, M. Y. Wang, M. J. Ricci and J. G. Liehr, Toxicol. Appl. Pharmacol. **145**, 54 (1997). The table above shows only an illustrative subset of the data.

[2] The rates are given per gram of protein in the microsomes, hence the funny units of v.

3. In noncompetitive inhibition, the inhibitor can bind either to the free enzyme, or to the enzyme-substrate complex:

$$\mathrm{E}+\mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \overset{k_{-2}}{\longrightarrow} \mathrm{E}+\mathrm{P}$$

$$\mathrm{E}+\mathrm{I} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{G}$$

$$\mathrm{C}+\mathrm{I} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{H}$$

The rate law for this inhibition mechanism is

$$v = \frac{v^0_{\mathrm{max}}[\mathrm{S}]}{[\mathrm{S}]\,(1+[\mathrm{I}]_0/K_4)+K_S\,(1+[\mathrm{I}]_0/K_3)},$$

where $v^0_{\mathrm{max}} = k_2[\mathrm{E}]_0$, $K_S = (k_{-1}+k_{-2})/k_1$, $K_3 = k_{-3}/k_3$ and $K_4 = k_{-4}/k_4$. Explain in detail how you could obtain estimates of v^0_{max}, K_S, K_3 and K_4 given noncompetitive inhibition data. [20 marks]

4. Derive a rate law for the sequential two-substrate enzyme-catalyzed reaction

$$\mathrm{E}+\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{F}$$

$$\mathrm{F}+\mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{G} \overset{k_{-3}}{\longrightarrow} \mathrm{E}+\mathrm{P}$$

Write your answer in terms of the rate constants, i.e. do not introduce the dissociation constants normally used in enzyme kinetics. [14 marks]