Chem 344 1st Hour Exam
Friday, Oct. 6, 2007, 2-3 PM

Closed book exam, only pencils and calculators permitted. No Computers. Put all of your work in the answer book. If you need graph paper we will provide it. If you use a calculator for graphical values like slope and intercept, you should fully explain your method, put in intermediate values and describe the result. "Floating" answers without substantiation receive little credit. Possibly useful information is at the end of the exam. ***Good Luck!!***

1. (20) A rule of thumb for simple reactions is that the rate can often double for a 10°C rise in temperature. If this is true for a reaction you are studying

A → Products

when you change between 25 °C and 35°C, for an initial concentration of **[A]** = 5mM, the rate changes from 2.5 x 10^{-7} Ms^{-1} to 5.0 x 10^{-7} Ms^{-1}

a. what would be the activation energy, E_a, for your reaction?
b. What is the pre-exponential factor, A?
c. what are $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$?
d. Would the rate also double if T changed from 85 °C and 95°C, why or why not?

2. (15) A reaction is described overall as:

A + 2B → 2C

The following table shows initial rates of formation of C for various reagent concentrations (in mM units, where mM = 10^{-3} M):

[A]	**[B]**	$\mathbf{V_0}$ ($mM{\cdot}s^{-1}$)
35	23	0.5 x10^{-3}
70	46	2.0 x10^{-3}
70	92	4.0 x10^{-3}

a. determine the empirical rate law in terms of formation of product **[C]** from this data, and clearly state your logic
b. state the overall order and the order with respect to each component
c. calculate the rate constant

3. (15) The hydrolysis of N-glutaryl-L-phenylalanine-p-nitoroanalylide (GPNA) to p-nitroaniline and N-glutaryl-L-phenylalanine is catalysed by α-chymotrypsin. The following data were obtained, where [S] is the concentration of GPNA, and $[E_0]$ = 4 x10^{-6} M:

[S] mM	0.25	0.50	1.0	1.5
$\mathbf{V_0}$ ($\mu M min^{-1}$)	2.2	3.8	5.9	7.1

Assume Michaelis-Menton kinetics and **determine values** for K_M, V_{max}, and k_2.
{recall: mM = 10^{-3} M and μM = 10^{-6} M}

4. (15) An enzyme contains a single ionizable group at its active site. For catalysis to occur, this group must dissociate, i.e. it must lose a H^+ to become the E^- form. The substrate bears a positive charge, S^+, which helps promote the formation of the enzyme-substrate complex, ES, with the negative enzyme, E^-. This is a proposed mechanism for this reaction:

$$\mathbf{EH \Leftrightarrow H^+ + E^-} \qquad \mathbf{(k_1 \text{ and } k_{-1})}$$

$$\mathbf{E^- + S^+ \Leftrightarrow ES} \qquad \mathbf{(k_2 \text{ and } k_{-2})}$$

$$\mathbf{ES \Leftrightarrow E + P} \qquad \mathbf{(k_3 \text{ and } k_{-3})}$$

a. H^+ is an inhibitor of the formation of P by this enzyme. What kind of inhibitor is it? Give a reason why.

b. Determine an expression for the initial rate in terms of E_0, S and H^+ for this mechanism. Show steps in derivation for full credit. Explain change from M-M result.

5. (20) A hypothetical reaction has the following stoichiometry:

$$\mathbf{A + B \Leftrightarrow Y + Z}$$

The following mechanism has been proposed:

$$\mathbf{A \Leftrightarrow X} \qquad (k_1 \text{ and } k_{-1})$$

$$\mathbf{X + B \rightarrow Y} \qquad (k_2)$$

a. Apply a steady state approximation and solve for a general rate law in terms of appearance of product, Y, that is consistent with the mechanism.

b. If k_2 is such that the second reaction is slow, and therefore the equilibrium is established rapidly in the first step, propose a reduction (simplification) of the mechanism

c. If k_2 is very fast compared to k_1 and k_{-1} , then how would that change the mechanism, what simplification would result?

d. Propose a method to test which case will be relevant for your experiment.

6. (15) Discussion questions—<u>but only short answers</u> (**Do only 3 of the following:**):

a. Explain the difference between order and molecularity in a reaction

b. Explain the difference between a transition state and a reaction intermediate

c. Use a reaction coordinate diagram to show the primary effect of an enzyme upon the energetics of a chemical reaction

d. Determine an expression for the half-life of a second order reaction: $r = k[A]^2$

e. Explain the difference between branching and propagation steps in a chain reaction

f. What kind of mechanistic steps are needed to get an overall 3/2 order in the reaction: $CO + Cl_2 \rightarrow COCl_2$

g. Explain the difference in the sources of the Arrhenius exponential term in activated complex theory and in collision theory