Chem 344 1st Hour Exam
Monday, Sept. 29, 2008, 2-3 PM

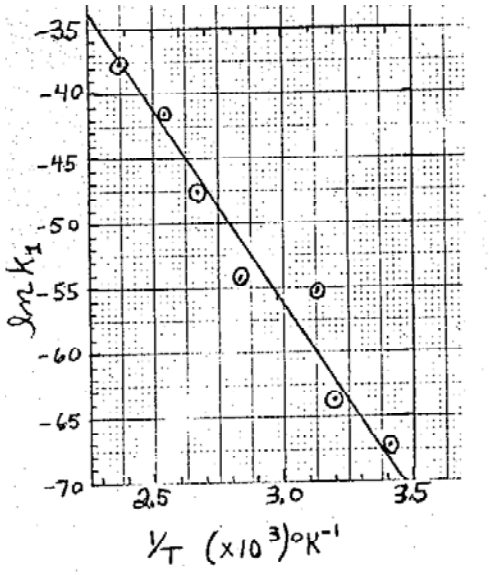
Closed book exam, only pencils and calculators permitted. No Computers. Put all of your work in the answer book. If you need graph paper we will provide it. If you use a calculator for graphical values like slope and intercept, you should fully explain your method, put in intermediate values and describe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

1. (20) The plot at right was made for the 1st order decomposition of chloroethane:

$H_3C\text{-}CH_2Cl \rightarrow H_2C{=}CH_2 + HCl$

a. Determine the activation energy and pre-exponential factor, A, for this reaction (use correct units)
b. Determine ΔH‡ and ΔS‡ for this reaction at 25°C
c. Do you think the student who did this experiment got it right? Why?

[note: temperatures are around room temp, 300 K, and ln k_1 is natural log, base e]



2. (25) In class we discussed the enzymatic mechanism for the peroxide decomposition to water. This is also catalyzed by HX (acid halide) without enzyme:

$$H_2O_2 \rightarrow 2\ H_2O + O_2$$ where HBr is the catalyst

A proposed mechanism is:

$$H_2O_2 + Br^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O + BrO^- \qquad (k_1, \text{slow})$$

$$H_2O_2 + BrO^- \xrightarrow{k_2} H_2O + O_2 + Br^- \qquad (k_2, \text{fast})$$

a. Determine a rate law for loss of H_2O_2 that is consistent with this mechanism.
b. What is the order with respect to H_2O_2 or Br^- ? (Hint: if reaction is run in water, $[H_2O]$ will be nearly constant.)
c. Describe any conditions under which the apparent rate law might change
d. Explain why Br^- can be seen to have something in common with an enzyme. Is your rate-law the same or different from a Michelis-Menton form for this reaction? Why?
e. Explain why k_{-2} is slow and why it is consistent to not be considered.

3. (15) The dephosphorylation of ATP is catalyzed by the enzyme myosin. From the following data, assuming the reaction behaves with typical M-M enzyme kinetics, determine the K_M and V_{max} values.

ATP_o (mM)	2	4	6	8	10
v_o ($x10^{-5}$ $M^{\bullet}s^{-1}$)	0.51	0.67	0.76	0.81	0.83

4. (20) In 1971 a report was published on the longevity of patients (sample of 81 males) diagnosed with congestive heart failure:

Time/years	0	1	3	5	7	9
Surviving/#	81	64	44	31	24	15

   a. Determine the rate law, give the form and order, and determine the rate constant. Be sure to properly express the variable (take care of units).
   b. Express the survivor number as a function of time (give an equation). Then use it to estimate the number after 12 years.
   c. Determine the half-life for survival.
   d. New drugs have been found that extend patient longevity for this diagnosis. Qualitatively describe how they might affect the kinetics of this process by postulating a hypothetical reaction coordinate diagram for some "reaction" that affects survival and show the effect of an effective drug on that coordinate diagram. (In Arrhenius terms, there are two possible brief answers, either is OK)

Choose only 2 of the following 3 kinetics questions (# 5, 6 or 7)—(10 – each)

5. Consider the following reaction

   A + B --> Products (k_f -->)

   a. If this reaction is 1st order in A and 2nd order in B write the overall rate law in terms of disappearance of A. What is the overall order?

   b. Describe how could you determine the rate of the reverse reaction?

6. A competitive inhibitor reversibly binds to the enzyme active site.
   a. Explain what mechanistic step this adds to the Michelis-Menton enzyme mechanism model.
   b. How will it affect the rate of the enzyme reaction? Does this appear in V_{max} or in K_m? How? (use of a Lineweaver-Burk plot may assist your answer)

7. The aldehyde form of glucose can be reversibly converted to both α- and β-glucose:

   Aldehyde + H_2O $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ α-glucose $\quad k_1 = 1.1x10^{2}\ sec^{-1}$, $k_{-1} = 7.6x10^{-3}\ sec^{-1}$

   Aldehyde + H_2O $\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$ β-glucose $\quad k_2 = 6.6x10^{1}\ sec^{-1}$, $k_{-2} = 2.7x10^{-3}\ sec^{-1}$

   If 1.0 mole of pure aldehyde is placed in 1.0 liter of water, what will be the equilibrium concentration of aldehyde, α-glucose and β-glucose ?