CE 561 Homework 1: Assigned 08/31/09, due 09/09/09

1) Send an email to me at swihart@buffalo.edu. In your message let me know (a) whether you plan to pursue an M.Eng., M.S., or Ph.D. degree; (b) at what colleges or Universities you previously studied, and (c) about how many semesters of undergraduate chemical kinetics and reaction engineering courses you took. If you wish, you may describe other things that you would like me to know about you, or any concerns you may have about this course.

2) Print, read and sign the Policy on Academic Honesty and Integrity. Submit it with your homework solutions.

3) What are the units of the rate constants of first-, second-, and third-order reactions if the concentrations are expressed in (moles per liter) and time is expressed in hours? What are the conversion functions that must be used to convert to concentration units of (molecules cm^{-3}) in each case?

4) Define the following: reaction rate, stoichiometric coefficient, reaction order, elementary reaction, overall reaction, molecularity, equilibrium constant, law of microscopic reversibility, Arrhenius plot, reaction mechanism, pseudo-steady-state approximation. Please put the definition in your own words. That is, do not simply copy the definition from the lecture notes, a textbook, or (especially) Wikipedia.

5) For the sequential reactions A→B with reaction rate $k_1 C_A$ and B→C with reaction rate $k_2 C_B$, derive expressions for the concentrations of A, B, and C as functions of time, starting with $C_A(t=0) = C_{Ao}$, $C_B(t=0) = C_C(t=0)=0$. Investigate limiting cases for $k_1 >> k_2$ and $k_2 >> k_1$.

6) For thermal cracking of ethane in a tubular reactor, the following data were obtained for the rate coefficient vs. temperature:

T(°C)	702	725	734	754	773	789	803	810	827	837
$k(s^{-1})$	0.15	0.273	0.333	0.595	0.923	1.492	2.138	2.718	4.137	4.665

Determine the activation energy and pre-exponential factor. Does this process obey the Arrhenius equation? Predict the rate coefficient at 1500 °C. How much does the predicted rate coefficient at 1500 °C change if the activation energy is increased or decreased by 5%?

7) Consider the following set of elementary reactions describing the reaction of hydrogen and bromine to give hydrogen bromide:

Initiation: $Br_2 \rightarrow 2\ Br$, with rate coefficient k_1
Propagation: $Br + H_2 \rightarrow HBr + H$, with rate coefficient k_2
$H + Br_2 \rightarrow HBr + Br$, with rate coefficient k_3
Inhibition: $H + HBr \rightarrow H_2 + Br$, with rate coefficient k_4
Termination: $2\ Br \rightarrow Br_2$, with rate coefficient k_5

This is a typical *free-radical chain reaction* in which each initiation reaction starts a sequence of fast propagation reactions involving highly reactive free radical species (in this case H and Br atoms). This sequence continues until it is ended by a termination reaction. Since these are elementary reactions, they all follow the law of mass action.

(a) Write the full set of rate equations for these reactions

(b) Simplify these rate equations by applying the pseudo-steady-state approximation to the concentrations of H and Br atoms

(c) How must the rate constants k_1 and k_5 be related to each other?

8) Solve the initial value problem

$$\frac{dx_1}{dt} = 2x_2, \qquad x_1(0) = 1,$$

$$\frac{dx_2}{dt} = -x_1 - 3x_2, \qquad x_2(0) = 1.$$

In other words, derive explicit formulas for the functions $x_1(t)$ and $x_2(t)$ that satisfy the preceding coupled differential equations and initial conditions. Then plot the trajectory $\left(x_1(t), x_2(t)\right)$ in the x_1,x_2 plane for $0 \le t \le 1$.

You may check your answer using Maple or a similar symbolic math package, but please work the solution out by hand, and show your work, to demonstrate that you are capable of doing so in a situation where Maple is unavailable (on an exam, for example).

Could this initial value problem represent two chemical reactions among two species? Explain why or why not.

9) Solve the initial value problem

$$\frac{d\underline{x}}{dt} = \underline{\underline{A}}\,\underline{x}, \qquad \underline{x}(0) = \underline{u}$$

with

$$\underline{\underline{A}} = \begin{pmatrix} 3/2 & -7/2 & 3/2 \\ -3/2 & -1/2 & 3/2 \\ 2 & -2 & 1 \end{pmatrix}, \qquad \underline{u} = \begin{pmatrix} 1 \\ 2 \\ 0 \end{pmatrix}$$

Again, you may check your answer using Maple or a similar symbolic math package, but please work the solution out by hand, and show your work, to demonstrate that you are capable of doing so in a situation where Maple is unavailable (on an exam, for example).