Chemistry 2710 Spring 2001 Assignment 2

Due: Friday, Jan. 26, 9:00 a.m.

Graphs: This and subsequent assignments and tests will require you to draw some graphs. The presentation standards for graphs in the lecture part of this course are as follows:

- Both computer-generated and hand-drawn graphs are acceptable. In the latter case, use graph paper with millimeter rulings. In either case, the graph should be at least $10\,\text{cm} \times 10\,\text{cm}$ in size.
- Axes must be labeled with the quantity plotted and (if appropriate) the units. Axis labels can be added by hand for computer-generated graphs.
- The endpoints of the two axes should be chosen so that the data cover a good portion of the graph.
- Data should be plotted with symbols (points, squares, whatever) which are large enough to be clearly visible but not so large as to make it unclear where the points are. Symbols with a radius of 1 mm are optimal. Slightly larger symbols are OK, but much larger symbols are just too small. Smaller symbols are fine if they are clearly visible (perhaps because they are in a different color).
- If the data are supposed to fit a line, that line should be drawn. A line should also be drawn if you want to show that the data *don't* fit a line particularly well.

Linear regressions: Recall that all slopes and intercepts are to be obtained from data by linear regression. You can use either a spreadsheet program or your calculator, but remember that you will only have access to your calculator in exams so make sure you know how to use it.

1. Suppose that we can measure the concentration of the reactant A in a reaction with stoichiometry $2\text{A} + \text{B} \rightarrow \text{P}$. In the first few seconds of the reaction, the observations are as follows:

t (s)	0.0	1.2	2.1	3.1	4.3	5.0
a (mol/L)	0.0400	0.0389	0.0381	0.0373	0.0364	0.0360

   (a) Do these data all lie in the initial rate region? If not, how many of these points can be used to determine the initial rate? Use one or more graphs to support your arguments. [5 marks]

   (b) Determine the initial rate of the reaction. [4 marks]

2. Iodine reacts with ketones (organic molecules containing a nonterminal C=O group) in aqueous solution according to the general reaction scheme

$$\mathrm{I_2} + \text{ketone} \rightarrow \text{iodoketone} + \mathrm{H^+} + \mathrm{I^-}.$$

For one particular ketone, the following initial rate data were obtained:

	$[\mathrm{I_2}]$ (mol/L)	[ketone] (mol/L)	$[\mathrm{H^+}]$ (mol/L)	v (mol L^{-1}s^{-1})
1	5×10^{-4}	0.2	1.0×10^{-2}	7.0×10^{-5}
2	3×10^{-4}	0.2	1.0×10^{-2}	7.0×10^{-5}
3	5×10^{-4}	0.5	1.0×10^{-2}	1.7×10^{-4}
4	5×10^{-4}	0.5	3.2×10^{-2}	5.4×10^{-4}

(a) What is the rate law for this reaction? [5 marks]

(b) Calculate the rate constant. [3 marks]

3. Suppose that the following initial rate data were obtained for a reaction A $\rightarrow$ B:

a (mol/L)	0.010	0.019	0.027	0.040	0.052
v (mmol L^{-1}s^{-1})	5.0	6.6	7.3	8.0	8.4

Can these data be described by a simple rate law? If so, calculate the order and rate constant. Otherwise, demonstrate that the data cannot be described by a simple rate law. [6 marks]

4. Consider the mechanism

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{B},$$
$$\mathrm{A} + \mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{C}.$$

(a) What is the overall reaction? [2 marks]

(b) Write down a complete set of mass-action differential equations. [6 marks]

(c) Relate the equilibrium constant for the overall reaction to the rate constants. [6 marks]

(d) Assuming that the reverse steps can be ignored and that the second step is much faster than the first, what rate law would be observed? [2 marks]

5. For the elementary reaction

$$\mathrm{H_{(g)}} + \mathrm{Br_{2(g)}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{HBr_{(g)}} + \mathrm{Br_{(g)}},$$

$k_1 = 2.09\times10^8\,\mathrm{L\,mol^{-1}s^{-1}}$ and the equilibrium constant is 1.5×10^{28}. What is k_{-1}? [4 marks]