Chemistry 2000B Spring 2002 Assignment 1

Due: Thursday, Jan. 24, noon

Notes on significant figures: In this and all subsequent assignments and tests in this course, you should report your answers to a reasonable number of significant figures. Slavish adherence to the significant figure rules is not required, but you may be penalized if your final answers have either way too many or way too few digits. One thing which is however quite important is keeping extra digits in intermediate steps of a calculation to prevent accumulated round-off errors from affecting your calculated values. You can either write down a few extra digits or use your calculator's memory to store intermediate results. Either way, your final answers should be *exactly* the same as mine to the number of digits displayed. To make sure that they are, use the molar mass table inside the front cover of your textbook in all assignments.

Notes on graphs: From time to time, we going to have to draw graphs in this class. For assignments, either hand-drawn or computer-generated graphs are acceptable. Obviously in tests you're going to have to draw your graphs by hand. If you have to produce a graph by hand for an assignment, use graph paper with a fine grid. However you produce them, they should be reasonably clearly labeled with the question number so that I don't have to guess what question a particular graph relates to. The axes should be labeled so that I know what you're plotting. Otherwise, I'm not too fussy provided your graph is *clear* and *accurate*.

Various bits of data can be extracted from a graph. Sometimes, we'll need to get a slope. At your level, it is perfectly acceptable to get two points off your line and to calculate a slope by $\Delta y/\Delta x$. However, the best way to get slopes from data is to use a statistical method called linear regression. Most scientific calculators have a linear regression function. If you know how to use yours and want to use regression instead of a direct graphical method, go ahead. Just make sure that you tell me you're doing that in your answers. In other words, never write down a number without giving me some indication of where it came from. This, of course, is good advice in general and not just for this one issue.

1. A 1.875 mol/L aqueous solution of sodium sulfate has a density of 1.2106 kg/L.

   (a) Calculate the molality of this solution. [6 marks]

   (b) Calculate the mole fraction of sodium in this solution. [4 marks]

2. For a reaction A $\rightarrow$ 2B at an initial concentration of A of 0.0431 mol/L, 1.42 μmol/L of B appears in the first 18.0 ms of the reaction. Calculate the initial rate of reaction. [3 marks]

3. Initial rate data are given below for the reaction $NH^+_{4(aq)} + NO^-_{2(aq)} \rightarrow N_{2(g)} + 2H_2O_{(l)}$.

Experiment	$[NH_4^+]$ (mol/L)	$[NO_2^-]$ (mol/L)	rate (mol L^{-1}s^{-1})
1	0.24	0.10	7.2×10^{-6}
2	0.12	0.10	3.6×10^{-6}
3	0.12	0.15	5.4×10^{-6}

Determine the rate law and rate constant for this reaction. [8 marks]

4. The gas-phase reaction of nitrogen monoxide with bromine proceeds by the following mechanism:

$$\mathrm{NO_{(g)} + Br_{2(g)} \xrightarrow{k_1} NOBr_{2(g)}}$$

$$\mathrm{NOBr_{2(g)} + NO_{(g)} \xrightarrow{k_2} 2NOBr_{(g)}}$$

   (a) Determine the overall reaction. [2 marks]

   Note: We haven't formally done this in class. What I'm basically asking you to do is to add the two reactions. You should have done this sort of thing in earlier courses.

   (b) Write down a full set of rate equations, i.e. an equation for the rate of change of the concentration of each of the four species in the mechanism. [4 marks]

   (c) It was once suggested that the first step in this reaction might be rate determining. The experimental rate law is $v = k[\mathrm{NO}]^2[\mathrm{Br_2}]$. Is the hypothesis that the first step is rate determining consistent with the experimentally observed rate law? Explain briefly. [4 marks]

   Note: When I say "explain briefly" (which I often do), I mean as briefly as possible while still addressing the relevant points. We may penalize you for including irrelevant material in your answers, so think about it a little before you set pen to paper.

   (d) Suppose that you wanted to confirm the experimental rate law by performing your own initial rate studies. Choose sets of experimental conditions which could be used for this purpose. Explain what patterns you would expect to see in your measurements. Make your answer as concrete as possible. [8 marks]

5. NOBr decomposes into nitrogen monoxide and bromine. At 10°C, the following data have been obtained:

t (s)	0	10	20	30	40
[NOBr] (mol/L)	0.0400	0.0303	0.0244	0.0204	0.0175

   (a) In a preliminary experiment which generated poor data, it was found that the reaction probably has a simple rate law with either a first or a second order dependence on the NOBr concentration. Which one is it? Also, calculate the rate constant. [10 marks]

   (b) How long would it take for the NOBr concentration to fall to 1% of the initial value? [2 marks]

   (c) Assuming that the mechanism is just the reverse of that shown in question 4, is there a rate-determining step? If so, what is it? [2 marks]