Chemistry 2710 Spring 2002 Test 2

Name: ____

Student number: ____________________

Aids allowed: Calculator. One $8\frac{1}{2} \times 11$-inch piece of paper containing any information you need. No other printed materials (e.g. periodic tables, calculator manuals) are allowed.

Instructions: Answer all questions in the spaces provided. If you run out of space for a particular question, you can use the backs of the pages but make sure to clearly label any continued work.

Graphs should be drawn on the graph paper attached and clearly labeled with the corresponding question number. You can use a graphing calculator instead of hand-drawn graphs, but you should in these cases provide a clearly labeled and reasonably accurate sketch of the graph.

Clarity may be considered in evaluating your answers. Make sure to explain in detail the procedures used to obtain the answers you present.

Possibly useful integrals:

$$\int \frac{dx}{x^2(a+bx)} = \frac{b}{a^2}\ln\left(\frac{a+bx}{x}\right) - \frac{1}{ax}$$
$$\int \frac{dx}{x(a+bx)^2} = \frac{1}{a^2}\ln\left(\frac{x}{a+bx}\right) + \frac{1}{a(a+bx)}$$

Question	1	2	3	4	5
Mark					

DO NOT OPEN THIS PAPER UNTIL INSTRUCTED TO DO SO.

1. Which of the following observations would be evidence for a complex reaction? Explain in a few words. [2 marks each]

   (a) The order of the reaction is different at different concentrations of reactants.

   (b) A reaction with the stoichiometry $\mathrm{A} \to \mathrm{B}$ has a rate law $v = ka^2$.

   (c) The rate is found to be proportional to $c^{1/2}$, where c is the concentration of a reactant.

2. When we use the steady-state approximation, we set $dc/dt = 0$ for one of the concentrations c. This does not mean that c is constant during the reaction. How would we calculate the true time rate of change of c after applying the SSA? [5 marks]

3. The experimental rate law for the reaction $2NO_{(g)} + Br_{2(g)} \rightarrow 2NOBr_{(g)}$ is $v = k[NO]^2[Br_2]$. Show that this rate law is consistent with the mechanism

$$\begin{aligned} NO_{(g)} + Br_{2(g)} &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOBr_{2(g)}, \\ NOBr_{2(g)} + NO_{(g)} &\overset{k_2}{\rightarrow} 2NOBr_{(g)}. \end{aligned}$$

Give an equation for the experimental rate constant k in terms of the elementary rate constants k_1, k_{-1} and k_2. Briefly discuss, based on your derivation of the rate equation, which elementary processes are fast and which are slow in this reaction. [10 marks]

4. In the last test, we discussed the first-order decay of the 2,5-dihydrofuran radical cation (2,5-DHF$^{+\bullet}$) in a CF_3CCl_3 matrix. First-order decay of radicals can result in one of two ways:

   (a) A unimolecular reaction occurs in which the radical rearranges itself. This is the case for 2,5-DHF$^{+\bullet}$ which rearranges to the radical cation 2,4-DHF$^{+\bullet}$ which is stable up to 140 K.[1]

   (b) The radical reacts with the matrix. The resulting process is really a pseudo-first-order reaction.

   These two possibilities are difficult to distinguish by kinetic methods alone.

   Radicals can also react by recombination, i.e. by a reaction of the type $R^\bullet + R^\bullet \rightarrow R_2$, or by other similar bimolecular reactions which pair up the odd electrons and produce nonradical products.

   The decay of 2,3-dihydrofuran radicals (DHF$^\bullet$) was studied by electron paramagnetic resonance (EPR) in a F-113 matrix[2] at 140 K. Recall that the intensity of an EPR signal is proportional to the concentration of the corresponding radical species. The results were as follows:[3]

t (min)	1.85	3.70	6.17	12.35	16.67	25.31	37.04
EPR intensity	0.71	0.56	0.43	0.30	0.25	0.18	0.13

   Based on these data, what is the likeliest mechanism for the removal of DHF radicals under the experimental conditions described above? [10 marks]

[1] The product 2,4-DHF$^{+\bullet}$ can be identified from its EPR spectrum.

[2] F-113 is the freon $CFCl_2CF_2Cl$.

[3] W. Knolle et al., J. Chem. Soc., Perkin Trans. 2, 2447 (1999).

5. Consider the reaction

$$2H_{2(g)} + 2NO_{(g)} \rightarrow 2H_2O_{(g)} + N_{2(g)}.$$

(a) Could this reaction be studied by monitoring the total pressure? Why or why not? [3 marks]

(b) The empirical rate law for the reaction is $v = k[H_2][NO]^2$. Derive an integrated rate law for this reaction with general initial conditions. Leave your answer in the form $t =$ something. [10 marks]

(c) At 700°C, $k = 0.384\,\mathrm{L^2 mol^{-2} s^{-1}}$. If the initial concentrations of hydrogen and of nitrogen monoxide are, respectively, 0.10 and 0.050 mol/L, how long would it take to consume 95% of the NO? [4 marks]