Chemistry 2710 Spring 2002 Test 1

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. Note that, because of the scale, calculator graphs are sometimes a little misleading so you use such a tool at your own risk.

Clarity may be considered in evaluating your answers. If you are asked a direct question, give a direct answer. Make sure to explain in detail the procedures used to obtain the answers you present. For instance, if you get a slope by performing a linear regression on your calculator, say so. If you determined something from a graph, refer to the graph in explaining your answer.

Question	Mark
1	
2	
3	
4	
5	

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1. ^{238}U decays by alpha emission. A natural sample of uranium weighing 0.0532 g produces 651 alpha particles per second. This sample is analyzed by mass spectrometry and found to contain 99.2832% ^{238}U and to have an average molar mass of 238.029 229 g/mol. What is the half-life of ^{238}U? Express your answer in years. Avogadro's constant is $6.022\,142\,0 \times 10^{23}\,\text{mol}^{-1}$. [10 marks]

2. For the reaction $CH_3NNCH_{3(g)} \rightarrow C_2H_{6(g)} + N_{2(g)}$, the following initial rate data have been obtained:

Experiment	$[CH_3NNCH_{3(g)}]$ (mol/L)	rate ($mol\,L^{-1}s^{-1}$)
1	2.4×10^{-2}	6.0×10^{-6}
2	8.0×10^{-3}	2.0×10^{-6}

(a) Determine the rate law and rate constant. [4 marks]

(b) Under the conditions of experiment 1, roughly how long would it take to make $10^{-4}\,mol/L$ of ethane ($C_2H_{6(g)}$)? [2 marks]

(c) Do you think that this reaction is elementary? Why or why not? [2 marks]

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

$$\mathrm{NO_{(g)} + Br_{2(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOBr_{2(g)}}$$

$$\mathrm{NOBr_{2(g)} + NO_{(g)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2NOBr_{(g)}}$$

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

(b) Relate the equilibrium constant for the overall reaction to the rate constants. [8 marks]

4. The radical cation of 2,5-dihydrofuran (2,5-DHF$^{+\bullet}$) can be generated by irradiation in a CF_3CCl_3 matrix at 77 K. The radical cation decays with first-order kinetics. It can be detected by electron paramagnetic resonance (EPR). The intensity of the EPR signal is proportional to concentration. The following data were obtained:[1]

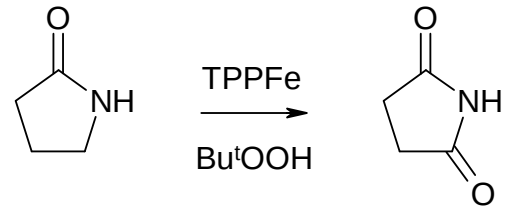
t (min)	2.6	3.4	4.4	5.4	6.9	8.4	10.1
EPR intensity	0.54	0.43	0.36	0.26	0.21	0.15	0.12

(a) Calculate the half-life of the radical cation. [8 marks]
Note: Because you know the order of the reaction, no graph is required.

(b) How long would it take for the 2,5-DHF$^{+\bullet}$ concentration to fall to 1% of its initial value? [2 marks]

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

5. Succinimide can be made by oxidation of pyrrolidone with tetraphenylporphyrinatoiron (III) chloride (TPPFe) and *tert*-butyl hydroperoxide (Bu^tOOH):



pyrrolidone succinimide

Varying only the concentration of pyrrolidone, the following initial rate data were obtained:[2]

[pyrrolidone] (mmol/L)	0.5	3.0	5.0	10.0
v (mmol $L^{-1}h^{-1}$)	0.908	3.86	5.98	6.52

Does this reaction have a simple rate law with respect to pyrrolidone and if so, what is the order? [10 marks]

[2] J. Iley et al., J. Chem. Soc., Perkin Trans. 2, 1299 (2001).