Chemistry 2000 Spring 2002 Midterm Examination

Name: _____

Student number: _____

Aids allowed: Calculator. No printed materials (e.g. periodic tables, calculator manuals) are allowed.

Formulas and data are given on page 7.

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. A hand-drawn graph should occupy at least half the sheet of graph paper. 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. If you use advanced features of your calculator to carry out a nontrivial computation (e.g. to solve a quadratic equation), say so. If you determined something from a graph, refer to the graph in explaining your answer.

Question	Mark
1	
2	
3	
4	
5	
6	
7	

DO NOT OPEN THIS PAPER UNTIL INSTRUCTED TO DO SO.

1. For the reaction $(CH_3N)_{2(g)} \rightarrow C_2H_{6(g)} + N_{2(g)}$, the following initial rate data have been obtained:

Experiment	$[CH_3NNCH_{3(g)}]$ (mol/L)	rate ($\text{mol}\,\text{L}^{-1}\text{s}^{-1}$)
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 $10^{-4}\,\text{mol/L}$ of ethane ($C_2H_{6(g)}$)? [2 marks]

Hint: This question can be answered very simply from the basic definition of rate.

2. In assignment 2, we analyzed certain aspects of the decomposition of benzylpenicillin (bp) under the assumption that the kinetics were first order. The following data were obtained at 180°C:

t (min)	2.21	5.16	13.26	22.84	40.52	60.41
% bp remaining	95	83	65	44	23	10

Are these data consistent with a first-order reaction? If so, what is the rate constant? [10 marks]

3. Fluorinated organic compounds are currently replacing chlorofluorocarbons as refrigerants and anaesthetics. Little is known of their atmospheric chemistry and, in particular, of their reactivity toward common stratospheric species such as hydroxide radicals. Consider the elementary reaction

$$OH_{(g)} + CF_3CH_2OCHF_{2(g)} \rightarrow \text{products}$$

for which the preexponential factor is $1.2 \times 10^{10}\,\text{L}\,\text{mol}^{-1}\text{s}^{-1}$ and the activation energy is 17.5 kJ/mol.

(a) Calculate the rate constant at -30°C, a typical stratospheric temperature. [2 marks]

(b) Write down a mass-action equation for the rate of change of the concentration of hydroxide radicals. [2 marks]

(c) Show that if the initial concentrations of the two reactants are equal, your rate equation reduces to a simple case studied in class. [2 marks]

(d) Suppose that, initially, $[OH] = [CF_3CH_2OCHF_{2(g)}] = 0.0405\,\text{mol/L}$. How long would it take for 90% of the hydroxide radicals to be used up at -30°C? [4 marks]

4. At 250°C, the equilibrium constant for the reaction $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ is 1.05. A mixture of 0.177 atm PCl_5, 0.223 atm PCl_3 and 0.111 atm Cl_2 is prepared. In which direction will the reaction proceed? [4 marks]

5. Calculate the pH of a $1.3 \times 10^{-4}\,\text{mol/L}$ aqueous solution of potassium hydroxide at 10°C. Report your answer to two decimal places. [4 marks]

6. Molecular bromine exists in equilibrium with bromine atoms in the gas phase:

$$\mathrm{Br}_{2(g)} \rightleftharpoons 2\mathrm{Br}_{(g)}.$$

When 1.05 mol of Br_2 is placed in 0.980 L flask at 1600°C, 1.20% of the bromine molecules dissociate. Calculate the equilibrium constant for this reaction. [10 marks]

7. Oxalic acid ($C_2O_4H_2$) is a diprotic acid whose two protons have K_a's of 6.5×10^{-2} and 6.1×10^{-5}, respectively. A 0.043 mol/L solution of oxalic acid in water at 25°C is prepared. What is the pH? Report your answer to two decimal places. [10 marks]

Useful information

For a first-order reaction, $\ln[\mathrm{R}] = \ln[\mathrm{R}]_0 - kt$.

For a second-order reaction, $\dfrac{1}{[\mathrm{R}]} = \dfrac{1}{[\mathrm{R}]_0} + kt$.

$k = k_\infty e^{-E_a/(RT)}$

$R = 8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}}$

$P^\circ = 1\,\mathrm{atm} = 101\,325\,\mathrm{Pa}$

$c^\circ = 1\,\mathrm{mol/L}$

$1\,\mathrm{m}^3 = 1000\,\mathrm{L}$

To convert degrees Celsius to Kelvin, add 273.15.

T (°C)	K_w
10	2.9×10^{-15}
25	1.0×10^{-14}