Chemistry 2710 Spring 2001 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) are allowed.

Additional data is given at the end of this paper.

Instructions: Answer all questions in the spaces provided. Use the backs of the printed pages for rough work or for extra space. Graphs should be drawn on the graph paper attached and clearly labeled with the corresponding question number.

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.

In the event that you use a graphing calculator instead of hand-drawn graphs, show at least a sketch of your graph with your answer. Be aware however that it is sometimes difficult to assign part marks if your sketch does not correspond to the expected graph.

DO NOT OPEN THIS PAPER UNTIL INSTRUCTED TO DO SO.

1. The decomposition of the ethoxy radical (CH_3CH_2O) has been studied in the gas phase at very low ethoxy radical pressures in the presence of helium.[1] The mechanism is a variation on the Lindemann mechanism:

$$CH_3CH_2O_{(g)} + He_{(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} He_{(g)} + CH_3CH_2O^*_{(g)}$$

$$CH_3CH_2O^*_{(g)} \overset{k_2}{\rightarrow} CH_2O_{(g)} + CH_{3(g)}$$

where $CH_3CH_2O^*$ is an energized radical.

   (a) Obtain an approximate rate law giving the dependence of the rate on the concentrations of reactants. [8 marks]

   (b) Show that at low pressures of helium, this rate law reduces to $v = k_1[\text{He}][CH_3CH_2O] = k_1'[CH_3CH_2O]$ where k_1' is a pseudo-first-order rate constant. [4 marks]

[1] F. Caralp et al., Phys. Chem. Chem. Phys. **1**, 2935 (1999).

(c) Measurements of the pseudo-first-order rate constant for the reaction at (known) low helium pressures therefore allow us to recover k_1. It was found that k_1 varies with temperature according to the Arrhenius law with a preexponential factor of $2.0 \times 10^{13}\,\mathrm{L\,mol^{-1}s^{-1}}$. Calculate the entropy of activation for the corresponding elementary reaction at 170°C, a typical temperature at which this reaction is studied. [6 marks]

2. Fluorescence quenching is a process in which a molecule transfers energy which would otherwise be released as fluorescence to another species in solution, called a quencher:

$$F^* + Q \xrightarrow{k_Q} F + Q^*.$$

The rate constants for quenching of the fluorescence of a charged polymer (AP90) by Tl^+ in water with potassium nitrate used to vary the ionic strength have been measured.[2] The results are as follows:

I (mmol/L)	0.46	2.11	3.90	7.20	13.67
$10^{-12}k_Q$ ($\text{L mol}^{-1}\text{s}^{-1}$)	2.26	0.85	0.56	0.34	0.22

Are these data consistent with the Brønsted-Bjerrum equation? If so, what is the effective charge[3] of the fluorescent group? [10 marks]

Note: The paper cited above does not give the temperature at which the experiments were performed. It seems likely, given the equipment used, that the temperature was uncontrolled. Since spectroscopic equipment is often a bit warmer than room temperature, assume that the experiments were carried out at 25°C.

[2] M.E. Morrison et al., J. Phys. Chem. **100**, 15187 (1996).

[3] It's an effective charge because the fluorescent groups are bound to a polymer. The charge may be somewhat delocalized over the polymer backbone, which makes the result a little less straightforward to interpret than the charge on a compact ion.

3. Aromatic compounds can be nitrated in strong acids according to the general reaction scheme

$$A + HNO_3 \rightarrow ANO_2 + H_2O.$$

The empirical rate law for these reactions is

$$v = k[A][HNO_3].$$

The rate constant for the nitration of *p*-chloronitrobenzene in 83.70% sulfuric acid has been measured at a few temperatures:[4]

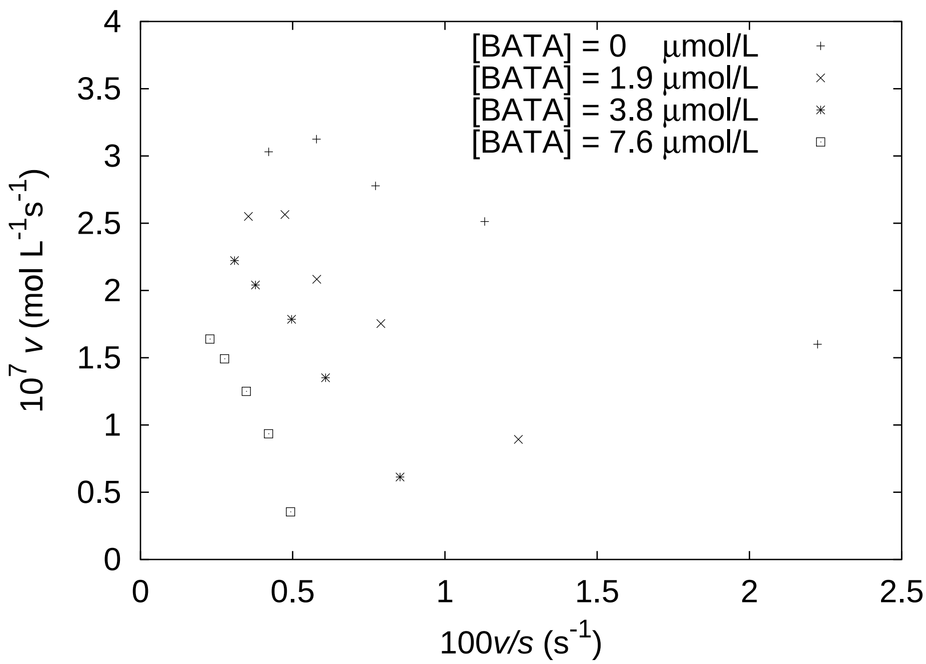
T (°C)	40	60	75
k ($\mathrm{L\,mol^{-1}s^{-1}}$)	6.9×10^{-4}	3.6×10^{-3}	0.43

Determine the preexponential factor and activation energy for this reaction. [8 marks]

Note: It is not necessary to draw a graph.

[4] N.C. Marziano et al., J. Chem. Soc., Perkin Trans. 2 **1998**, 1973 (1998).

4. Many of the most commonly used antibiotics are members of a class of biochemical compounds called β-lactams. Antibiotic resistance in bacteria is often associated with the expression of a β-lactamase, an enzyme which hydrolyzes β-lactams. One possible method for combating antibiotic resistance is to include a β-lactamase inhibitor with the antibiotic. This would reduce the effectiveness of the lactamase and thus allow the antibiotic to do its job. As a step in this direction, Yang and Crowder have studied the inhibition of the hydrolysis of nitrocefin by a lactamase from *Stenotrophomonas maltophilia* by N-benzylacetyl-D-alanylthioacetic acid (BATA).[5] Nitrocefin is a β-lactam which is not used as an antibiotic but has spectroscopic properties which make it particularly suitable for enzyme assays. Based on a Lineweaver-Burk plot, Yang and Crowder concluded that BATA is a competitive inhibitor. Yang and Crowder's results are shown below, plotted in Eadie-Hofstee form:



Do you agree that BATA is a competitive inhibitor? Explain. [6 marks]

[5] K.W. Yang and M.W. Crowder, Arch. Biochem. Biophys. **368**, 1 (1999).

Data

$R = 8.314\,510\,\mathrm{J\,K^{-1}mol^{-1}}$

$h = 6.626\,069 \times 10^{-34}\,\mathrm{J/Hz}$

$1\,\mathrm{bar} = 100\,000\,\mathrm{Pa}$

$k_B = 1.380\,658 \times 10^{-23}\,\mathrm{J/K}$

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

To convert degrees Celsius to Kelvin, add 273.15.

The permittivity of water at 25°C is $6.954 \times 10^{-10}\,\mathrm{C^2N^{-1}m^{-2}}$.