Chemistry 2740 Spring 2008 Final Examination

Time: 3 h

Marks: 115

Aids permitted: calculator, one 8.5 × 11-inch formula sheet

Answer all questions in the booklets provided.

Necessary data are given on page 5.

This exam consists of 3 sections. Answer all questions in section 1. In sections 2 and 3, answer only the required number of questions. Extra answers will not be marked. If you attempt a question and later decide not to have it marked, cross it out.

1 Answer *all* questions in this section.

Value of this section: 97

1. For each of the following statements, indicate whether it is true or false and, **in a few words**, explain your reasoning. [2 marks each]
   (a) A bomb calorimeter measures $\Delta_r H$.
   (b) Exothermic reactions are always spontaneous.
   (c) According to Debye-Hückel theory, the activity coefficient of a solute depends on its charge, so all uncharged solutes have an activity coefficient of 1.
   (d) The rate of a reaction with overall stoichiometry A → 2B is $\frac{1}{2}\frac{d[\mathrm{B}]}{dt}$.
   (e) The gas-phase reaction $CH_3N{=}NCH_3 \rightarrow C_2H_6 + N_2$ is not elementary.
   (f) The activation energy of an elementary reaction can't be negative.
   (g) The encounter pair in the theory of bimolecular reactions in solution is a transition state for the reaction.

2. Given the usual kinds of data tables, how could you calculate the maximum electrical work per mole of reactants which could be performed at 25°C by a given electrochemical cell? Outline one possible calculation method, indicating what data you would have to look up. [4 marks]

3. Equilibrium constants are related to rate constants for the underlying elementary processes. Rate constants always increase with increasing temperature, while equilibrium constants can increase or decrease with temperature. Why is this possible? [4 marks]

4. Calculate the base ionization constant of the hydrogen phosphate ion at 80°C, i.e. the equilibrium constant for the transfer of a proton from water to the hydrogen phosphate ion. [10 marks]

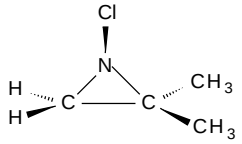
5. When a carbonate solution is acidified, carbon dioxide is produced.

   (a) Can we predict the sign of the entropy change in this process without doing any calculations? If so, predict the sign. In either event, explain your reasoning. [4 marks]

   (b) Calculate the standard entropy change for the reaction of carbonate ions with hydrogen ions producing carbon dioxide. [6 marks]

6. Enantiomers can often be separated by gas chromatography, using columns packed with a chiral stationary phase. It is also possible to study the kinetics of interconversion between two enantiomers in a gas chromatograph. There are a number of techniques which can be used, ranging from a "stopped-flow" method in which the flow of carrier gas is stopped to allow time for the reaction to occur inside the column, to dynamic methods which require the analysis of chromatogram peak shapes.[1] The chiral stationary phase may affect the kinetics of the reaction due to binding of the material being studied to the stationary phase. However, this is a minor disadvantage to a relatively easy experimental method for studying the interconversion between two enantiomers in the gas phase.

   (a) Mydlová has measured the rate constant for the interconversion between the two enantiomers of 1-chloro-2,2-dimethylaziridine by dynamic reaction gas chromatography in a setup with coupled ChiralDex BTA and polydimethylsiloxane columns.[2] The R isomer is illustrated below:



   The reaction involves inversion of the configuration at the nitrogen atom. The data given below are averages of two estimates of the rate constant, assuming that $K = 1$ for the interconversion process:

T/K	338	348	358	368
$k/10^{-4}\,\mathrm{s}^{-1}$	0.8	1.8	3.2	9.4

   Calculate the activation energy and preexponential factor for this interconversion. [12 marks]

   (b) Calculate the entropy of activation at 25°C. What does the value of the entropy of activation tell us about this reaction? [6 marks]

[1] J. Krupčik et al., *J. Chromatogr. A* **1186**, 144 (2008).
[2] Data reported in J. Krupčik et al. (2008), cited above.

7. (a) Ethanol (C_2H_5OH) reacts with the dichromate ion ($Cr_2O_7^{2-}$) in acidic solution to produce ethanal (acetaldehyde, C_2H_4O) and the chromium(III) ion. Balance the reaction. [6 marks]

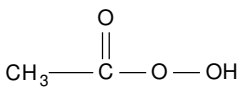
   (b) Calculate the standard reduction potential corresponding to the ethanal/ethanol half-reaction obtained above. [8 marks]

   Hint: Start by calculating the reversible voltage under standard conditions for the electrochemical cell

$$Pt_{(s)}|H_{2(g)}|H^+_{(aq)}\|C_2H_4O_{(aq)}, C_2H_5OH_{(aq)}, H^+_{(aq)}|Pt_{(s)}.$$

   (c) Calculate the standard free energy of formation of the aqueous chromium(III) ion. [8 marks]

8. Peracetic acid (PAA) is the following compound:



   Recently, Zhao and coworkers have proposed the following mechanism for the decomposition of peracetic acid in aqueous solution at elevated temperatures:[3]

   - First, PAA is protonated on the carbonyl oxygen, creating a carbocation:

$$PAA + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PAAH^+.$$

   - The carbocation forms an intermediate addition product with another PAA:

$$PAAH^+ + PAA \overset{k_2}{\rightarrow} X + H^+.$$

   - The intermediate decomposes to acetic acid (symbolized AH), acetate (A^-), a proton and oxygen:

$$X \overset{k_3}{\rightarrow} AH + A^- + H^+ + O_2$$

   - Finally, the acetate reprotonates:

$$A^- + H^+ \overset{k_4}{\rightarrow} AH.$$

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

   (b) Protonation and deprotonation steps are extremely fast in aqueous solution. Using this information and any reasonable additional assumptions you find necessary, determine the rate law for this reaction. [10 marks]

   (c) What is the order of the reaction with respect to PAA? [1 mark]

   (d) What would you predict the effect of raising the pH on the reaction rate to be? [2 marks]

[3] X. Zhao et al., *J. Mol. Catal. A: Chem.* **284**, 58 (2008). I have changed their numbering of the steps for convenience, and expanded one of their steps.

2 Answer any *two* questions from this section.

Value of this section: 8 marks

In your exam booklet, clearly mark which question you are answering. Remember that extra answers from this section will **not** be marked.

1. When we make ice cream using liquid nitrogen, the liquid nitrogen fulfills two roles leading to desirable properties of the final product. What are they? [4 marks]
2. Briefly describe the Loschmidt experiment for measuring diffusion coefficients of gases. [4 marks]
3. Briefly describe the flash photolysis experiment. [4 marks]
4. What is heat? [4 marks]
5. The Helmholtz free energy can be used to obtain two different pieces of information about a process. What are they? Be precise about the relationship between the information wanted and how it is obtained from the Helmholtz free energy. [4 marks]

3 Answer *one* question from this section.

Value of this section: 10 marks

In your exam booklet, clearly mark which question you are answering. Remember that extra answers from this section will **not** be marked.

1. While cooking a beef roast recently, I recorded the following data: The oven temperature was 175°C. I recorded the internal temperature of the roast at various times (given as hours and minutes p.m.) during the cooking process.

Time	4:28	4:37	4:53	5:13	5:25	5:33
T/°C	3	6	19	39	51	60

   The experiment stopped at 5:33 p.m. because the internal temperature had reached the medium-rare point. Do these data obey the usual first-order rate law for warming? [10 marks]

2. Anikeev, Ermakova and Goto have studied the decomposition reaction of nitromethane in supercritical water.[4] Specifically, they measured the fraction of the initial nitromethane converted to *product* as a function of reaction time at a temperature of 664 K and a pressure of 272 atm:

t/s	0	45	67	134	270	467
X	0	0.381	0.537	0.763	0.951	0.994

   Show that the reaction obeys first-order kinetics, and determine the rate constant. [10 marks]

[4] Anikeev et al., *Kinet. Catal.* **46**, 821 (2005).

Useful data

$\mathcal{F} = 96\,485.342\,\mathrm{C/mol}$

$h = 6.626\,068\,8 \times 10^{-34}\,\mathrm{J/Hz}$

$k_B = 1.380\,650\,3 \times 10^{-23}\,\mathrm{J/K}$

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

To convert degrees Celsius to Kelvin, add 273.15.

Standard thermodynamic data at 1 bar and 25°C

Species	$\frac{\Delta_f \bar{H}^\circ}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta_f \bar{G}^\circ}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\bar{C}_p}{\mathrm{J\,K^{-1}mol^{-1}}}$
$CO_{2(g)}$	−393.51	−394.37	37.1
$CO^{2-}_{3(aq)}$	−675.23	−527.90	
$C_2H_4O_{(aq)}$	−212.34	−139.00	
$C_2H_5OH_{(aq)}$	−276.98	−180.85	
$Cr_2O^{2-}_{7(aq)}$	−1490.3	−1301.1	
$HPO^{2-}_{4(aq)}$	−1299.0	−1096.0	
$H_2O_{(l)}$	−285.830	−237.140	75.40
$H_2PO^{-}_{4(aq)}$	−1302.6	−1137.2	
$OH^{-}_{(aq)}$	−230.015	−157.220	

Standard reduction potentials at 298.15 K	
Reduction process	$\mathcal{E}^\circ$/V
$Cr_2O^{2-}_{7(aq)} + 14H^{+}_{(aq)} + 6e^{-} \rightarrow 2Cr^{3+}_{(aq)} + 7\,H_2O_{(l)}$	+1.33