Chemistry 2740 Spring 2009 Final Examination

Time: 3 hours
Marks: 105
Aids allowed: calculator, 8.5×11-inch formula sheet
Instructions: You can answer the questions in any order, but make sure that you clearly label each of your answers with the section and question number in your exam booklet(s).
In questions whose answer requires the analysis of a graph, please sketch the graph.
In section 2, you have a selection of questions. **Do not answer more than the required number of questions.** I will stop marking as soon as I have reached the required number of questions from this section. **Extra answers will not be marked.** If you answer extra questions, make sure you cross out the ones you don't want me to mark.

Data

$e = 1.602\,176\,46 \times 10^{-19}\,\mathrm{C}$
$F = 96\,485.342\,\mathrm{C/mol}$
$k_B = 1.380\,650\,3 \times 10^{-23}\,\mathrm{J/K}$
$L = 6.022\,142\,0 \times 10^{23}\,\mathrm{mol^{-1}}$
$R = 8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}}$
To convert degrees Celsius to Kelvin, add 273.15.

Standard thermodynamic data at 298.15 K			
Species	$\frac{\Delta_f H^\circ}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta_f G^\circ}{\mathrm{kJ\,mol^{-1}}}$	$\frac{C_{p,m}}{\mathrm{J\,K^{-1}mol^{-1}}}$
$F^-_{(aq)}$	−335.35	−281.52	
$H_2O_{(l)}$	−285.830	−237.140	75.40
$SF_{6(g)}$	−1220.47	−1116.44	96.88
$SO^{2-}_{4(aq)}$	−909.34	−744.00	

Standard reduction potentials at 298.15 K	
Reduction process	E°/V
$Cd^{2+}_{(aq)} + 2e^- \rightarrow Cd_{(s)}$	−0.4030
$Li^+_{(aq)} + e^- \rightarrow Li_{(s)}$	−3.0401

1 Answer *all* questions in this section.

Value of this section: 85 marks

1. What is the first law of thermodynamics? [1 mark]

2. If we say, for a particular process on a particular system, that $w = -5\,\mathrm{J}$, what does that mean? [1 mark]

3. SF_6 is inert under most conditions. For example, it won't undergo hydrolysis:

$$\mathrm{SF_{6(g)} + 4H_2O_{(l)} \not\rightarrow 6F^-_{(aq)} + SO^{2-}_{4(aq)} + 8H^+_{(aq)}}.$$

   Is the above reaction thermodynamically allowed at 25°C when the pressure of SF_6 is 0.2 bar, the concentration of fluoride ions is 1.0×10^{-3} mol/L, the concentration of sulfate is 0.43 mol/L, and the pH is 6.0? Does this agree or disagree with the empirical observation that SF_6 can't be hydrolyzed? Discuss briefly. [7 marks]

4. Consider the following simple electrochemical cell:

$$\mathrm{Cd_{(s)}|CdCl_{2(aq)}(0.50\,mol/L)\|LiCl_{(aq)}(0.80\,mol/L)|Li_{(s)}}.$$

   At 25°C, the mean ionic activity coefficient of $CdCl_2$ at a concentration of 0.50 mol/L is 0.1006, and the mean ionic activity coefficient of LiCl at 0.80 mol/L is 0.755. What emf does this cell generate at 25°C, and in what direction do electrons flow? [9 marks]

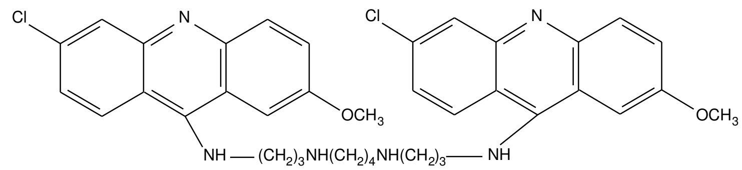
5. The designer drug *N*-methyl-benzodioxolyl-butanamine (MBDB) is metabolized by members of the cytochrome P450 family of isozymes [closely related enzymes that catalyze the same reaction(s)]. A variety of products are obtained, one of which is 1,2-dihydroxy-4-[2-(methylamino)butyl]benzene (DHMBB). The following initial rate data were obtained for the transformation of the R stereoisomer of MBDB by the P450 isozyme CYP2B6 to DHMBB:[1]

[R-MBDB]/μmol L^{-1}	21	55	100	132	258	452	585	845
v/mol min^{-1}(mol enzyme)$^{-1}$	0.65	1.17	1.94	2.01	2.73	2.73	2.98	3.02

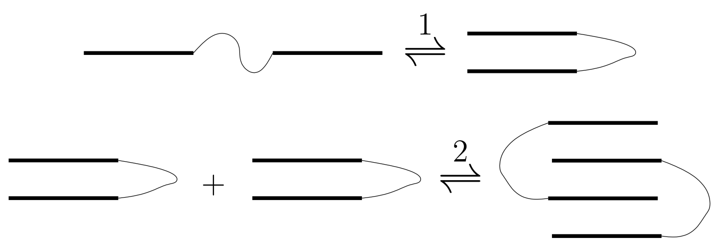
   Calculate $v_{\max}$ and K_M for this enzyme. [9 marks]

[1] M. R. Meyer et al., *Biochem. Pharmacol.* **77**, 1725 (2009).

6. In aqueous solution, the acridine homodimer (AcrH)



can exist either in an unfolded form or in a folded conformation where the two ring systems stack on top of each other. The folded AcrH molecules can also form aggregates in which the ring systems from different molecules interleave. Schematically, we have



In this diagram, the heavy straight lines represent the ring systems, which we are viewing from the side. Further aggregation reactions are possible involving additional AcrH molecules. However, for the purposes of this question, we will assume that only these two reactions are significant.

(a) Evstigneev and coworkers have measured the equilibrium constant for the folding process (reaction 1) at 298 K and at 308 K.[2] They found $K_{298} = 42$ and $K_{308} = 26$. Calculate

i. the standard enthalpy of reaction,

ii. the standard free energy of reaction, and

iii. the standard entropy of reaction.

Does the sign of the entropy change make sense? Explain briefly. [8 marks]

(b) For the dimerization reaction (reaction 2), Evstigneev and coworkers found $\Delta_r H^\circ = -32$ kJ/mol. Find the overall enthalpy change for the process which takes unfolded AcrH and creates the two-molecule aggregate. [4 marks]

(c) The equilibrium constant for reaction 2 at 298 K is 540. Suppose that we dissolve 5.0×10^{-4} mol/L of AcrH in water. At equilibrium at 298 K, what are the concentrations of the unfolded molecule, folded AcrH, and the two-molecule aggregate? [12 marks]

Hint: You have three unknowns, so you need three equations. The first two equations should be obvious. One way to get a third equation is to consider that the total amount of AcrH in solution is constant.

[2] M. P. Evstigneev et al., *J. Mol. Struct.* **784**, 162 (2006).

7. Volatile organic compounds in the atmosphere can be oxidized by NO_3, often yielding undesirable products (e.g. toxic compounds). These reactions often happen in water droplets rather than in the gas phase. Gaillard de Sémainville and coworkers have studied the reactions of NO_3 with some ketones, aldehydes and carboxylic acids in aqueous solution.[3] In their experiments, NO_3 was generated by laser flash photolysis.

   (a) In one set of experiments, peroxodisulfate anions ($S_2O_8^{2-}$) were photolyzed to SO_4^- radical ions using a laser flash at 351 nm. The SO_4^- ions then reacted with nitrate ions to yield sulfate ions and NO_3. The reaction of NO_3 with either a carboxylic acid or its conjugate base was then followed spectroscopically by recording the absorbance of the solution at a wavelength where NO_3 absorbs strongly (632.8 nm).

      i. Briefly explain how the laser flash photolysis experiment works, with specific reference to this reaction system. Make sure to explain what solution(s) must be prepared. Do the reactions have to satisfy any special conditions in order for the measurements described above to give the rate of reaction of NO_3 with an organic compound? [9 marks]

      ii. Suppose that the reaction of SO_4^- with nitrate is diffusion-limited. Estimate the rate constant of this reaction at 298 K assuming that the diffusion coefficients of SO_4^- and of nitrate are both about $2 \times 10^{-9}\,\mathrm{m^2/s}$, and that the radii of the two ions are both about 2×10^{-10} m. The permittivity of water at this temperature is $6.957 \times 10^{-10}\,\mathrm{C^2\,N^{-1}m^{-2}}$. [5 marks]

   (b) The reaction of NO_3 with an organic compound in aqueous solution displays a simple rate law, $v = k[NO_3][R]$, where R stands for the organic reactant. NO_3 is a highly reactive radical, so it will typically react with other compounds in solution, yielding an additional "background" decay which obeys first-order kinetics. In these experiments, the organic reactant was present in great excess over the NO_3 generated by flash photolysis. Explain why the data from these experiments would be consistent with a first-order rate law, and give an equation for the observed rate constant. Then show that the second-order rate constant for the reaction of NO_3 with R is the slope of a graph of the observed first-order rate constant vs [R]. [4 marks]

   (c) The following data were obtained for the reaction of excess lactic acid (R) with NO_3 at 298 K:

$[R]/\mu\mathrm{mol\,L^{-1}}$	100	300	500	700	900
$k_{obs}/\mathrm{s^{-1}}$	620	911	1091	1142	1535

   Determine the second-order rate constant for the reaction of lactic acid with NO_3. [6 marks]

[3] Ph. Gaillard de Sémainville et al., *Phys. Chem. Chem. Phys.* **9**, 958 (2007).

(d) The following second-order rate constants were recovered for the reaction of lactic acid with NO_3:

T/K	278	288	298	308	318
$k/10^6\,\mathrm{L\,mol^{-1}s^{-1}}$	0.74	0.84	2.06	2.75	2.59

Determine the activation energy and preexponential factor of the reaction. [10 marks]

2 Answer any *four* questions in this section.

Value of this section: 20 marks

1. During a coop work term, you end up working in quality control at an ice cream factory. You discover (by random sampling) that one batch has a grainy consistency. What part(s) of the production process should you look for problems in, and why? [5 marks]

2. What are initial rate experiments and why are they useful? [5 marks]

3. List three different ways to determine by calculation whether a given reaction is or is not thermodynamically allowed. For each method you list, indicate whether the method works in general, or only under special conditions. [5 marks]

4. Explain why the law of microscopic reversibility is required to make kinetics consistent with thermodynamics. [5 marks]

5. Consider the gas-phase reaction A + B → C. Sketch the probable entropy profile for this reaction against the reaction coordinate. Label your sketch with the quantities $\Delta_r S$ and $\Delta^{\ddagger} S$. [5 marks]

6. What is a chain reaction? What are the necessary mechanistic features of a chain reaction? [5 marks]

7. Explain how the cell

$$\mathrm{Pt_{(s)}|H_{2(g)}|H^+_{(aq)}\|CuCl_{2(aq)}|Cu_{(s)}}$$

could be used to measure the mean ionic activity coefficient of copper (II) chloride. Treat the pH and pressure of H_2 in the left half-cell, and the concentration of copper (II) chloride in the right half-cell as known quantities. [5 marks]

8. Describe one method for measuring a diffusion coefficient. [5 marks]