Chemistry 2740 Spring 2010 Final Examination

Time: 3 hours
Marks: 105
Aids allowed: calculator, 8.5×11-inch formula sheet
Useful data is given on the back page of this exam.
Instructions: Answer all questions in section 1. In sections 2 and 3, answer only the required number of questions. Extra answers will *not* be marked. Cross out any work you don't want me to mark.
You can answer the questions in any order, but make sure that you clearly label each of your answers with the question number in your exam booklet(s).
If you use a graph to answer a question, make sure to provide a reasonable sketch of the graph, as well as a brief explanation of what information the graph provides.

1 Answer *all* questions in this section.

Value of this section: 79

1. In the textbook, I avoided the commonly used word "spontaneous" in the section on thermodynamics, preferring the phrase "thermodynamically allowed". Why? [2 marks]

2. Explain why the law of microscopic reversibility is required to make kinetics consistent with thermodynamics. [2 marks]

3. What is an initial rate experiment? Briefly discuss the advantages and disadvantages of initial rate experiments. [6 marks]

4. Explain the physical origin of the phenomenon of transmembrane potential. [8 marks]

5. The solubility of calcium carbonate in water is 1.53×10^{-4} mol/L at 25.0°C and 1.90×10^{-4} mol/L at 75.0°C. The relative permittivity of water at 25.0°C is 78.37, and at 75.0°C it is 62.36.

   (a) Calculate the mean ionic activity coefficient of calcium carbonate in each of these solutions. [8 marks]

   (b) Estimate the enthalpy of solution of this compound, taking into account the nonideal behavior of calcium carbonate in water. [6 marks]

   (c) Estimate the standard enthalpy and standard free energy of formation of an aqueous calcium ion, again taking nonideal effects into account. [8 marks]

6. *Aplysia dactylomela* is a species of sea hare (a type of sea slug) that reproduces very rapidly. *A. dactylomela*'s diet consists of a variety of algae. In one set of lab experiments, *A. dactylomela* was fed a diet of *Cladophora*, a green algae.[1] The animals were weighed before the experiment, then again at the end. They were then dried in an oven. The percentage of the body weight that was water was assumed to be constant throughout the experiment, so the gain in dry weight could be estimated. Any offspring produced were also dried and weighed. Finally, feces were collected and dried. The dried animals, offspring and feces were analyzed by bomb calorimetry to determine their energy content. When dealing with whole animals, some percentage of the material is non-combustible, and shows up as ash after opening the calorimeter. Calculations of metabolic energy are only concerned with the material that can be burned, so the non-combustible ash component, reported as a percentage of the dry mass, must be excluded from the mass of the biological materials in the calculations. The following data were obtained:

		Animal			Offspring			Feces		
Duration of experiment/days	Energy content of food/kcal	Increase in dry mass/g	Ash/%	Specific combustion energy / kcal (g ash-free material)$^{-1}$	Dry mass/g	Ash/%	Specific combustion energy / kcal (g ash-free material)$^{-1}$	Dry mass/g	Ash/%	Specific combustion energy / kcal (g ash-free material)$^{-1}$
14	27.92	2.21	33	4.666	0.39	31	4.920	23.50	76	3.220

How much energy did the animals use per day for metabolism and physical activity? [7 marks]

7. Some enzymes have an inactive form that is in equilibrium with the active form, i.e. the mechanism includes, along with the usual Michaelis-Menten reaction steps, a reversible step

$$\mathrm{E} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{X},$$

where X is the inactive form of the enzyme. Derive a rate law for catalysis of an isomerization reaction $\mathrm{S} \rightarrow \mathrm{P}$ by an enzyme with this characteristic. Clearly identify $v_{\max}$ and K_M. [16 marks]

[1] T. H. Carefoot, *J. Exp. Mar. Biol. Ecol.* **5**, 47 (1970).

8. (a) Enzyme kineticists often discuss the quantity $k_{cat} = v_{max}/e_0$. Assuming that a reaction obeys the Michaelis-Menten mechanism, to what rate constant, or combination of rate constants, does k_{cat} correspond? [1 mark]

   (b) The enzyme chorismate mutase catalyzes one reaction step in the biosynthesis of phenylalanine and tyrosine in bacteria, fungi and plants. Kast, Asif-Ullah and Hilvert have measured k_{cat} for this enzyme at different temperatures, and obtained the following data:[2]

T/K	278	288	298	308	318
k_{cat}/s^{-1}	6.54	15.7	33.8	69.9	130

   Calculate the activation energy and preexponential factor. [10 marks]

   (c) Calculate the entropy of activation at 25°C. Assuming a simple Michaelis-Menten reaction, what does the sign and/or value of the entropy of activation tell you about the reaction for which k_{cat} is the rate constant? [5 marks]

2 Answer *one* question in this section.

Value of this section: 10 marks

1. The properties of complex materials are typically influenced both by their composition and by their processing, i.e. by the exact sequence of steps used to manufacture the finished product. Discuss this statement, using the manufacture of ice cream as an example. [10 marks]

2. Suppose that you are studying a competitive inhibitor of an enzyme. The inhibitor is fluorescent, but its fluorescence is quenched (i.e. it doesn't fluoresce) when bound to the enzyme, so the concentration of the inhibitor can be followed by fluorescence measurements. You would like to determine the rate constants for association and dissociation of the enzyme-inhibitor complex, as well as K_I. What experiment(s) could you do to get these parameters? Describe the experiment(s) briefly, including a description of the solution(s) that would have to be prepared. Also explain what data would be collected and how the parameters would be obtained. [10 marks]

[2] P. Kast, M. Asif-Ullah and D. Hilvert, *Tetrahedron Lett.* **37**, 2691 (1996).

3 Answer *one* question in this section.

Value of this section: 16 marks

1. (a) The viscosity of a liquid typically decreases with increasing temperature. This temperature dependence is sometimes described using the Arrhenius-like equation

$$\eta = A_\eta \exp\left(\frac{E_\eta}{RT}\right).$$

   Note the lack of a negative sign in the exponential. Using any relevant theories, determine how the activation energy of a diffusion-controlled reaction between neutral molecules is related to the "activation energy" of viscosity. [12 marks]

   Hints: The size of a solute molecule depends very little on temperature and should be treated as a fixed quantity. To figure out the activation energy, take $d(\ln k)/dT$ both for the Arrhenius equation and for your expression for the rate constant.

   (b) The viscosity of water is 1.79 mPa s at 0°C, and 0.28 mPa s at 100°C. What is the value of E_η for water? [4 marks]

2. Many marine organisms contain a substantial amount of calcium carbonate, either as a shell or as skeletal elements. Shells can be removed, but other skeletal elements are often less easy to separate from the soft tissues. Moreover, depending on the diet of the organism, a substantial amount of calcium carbonate can end up in feces. When we carry out bomb calorimetry on marine organisms or their feces, the following reaction occurs:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}.$$

   This reaction does not correspond to any biological oxidation so, if we want to use calorimetry to calculate the amount of energy an organism has stored, the amount of calcium carbonate in the sample must be analyzed, and a correction must be made to the raw calorimetric results corresponding to the heat of this reaction. Incidentally, such corrections are included in the data presented in question 6 from section 1.

   (a) The initial and final temperatures in a bomb calorimeter are both close to 25°C. Show that this reaction is not thermodynamically allowed at this temperature in the presence of 39 Pa of carbon dioxide (the atmospheric partial pressure of this gas). That being the case, why is this reaction relevant anyway? [9 marks]

   (b) Calculate the correction to the measured heat per gram of calcium carbonate in the sample. Explain briefly how you would use this correction. The molar mass of calcium carbonate is 100.09 g/mol. [7 marks]

Useful data

$\epsilon_0 = 8.854\,187\,817 \times 10^{-12}\,\mathrm{C^2 J^{-1} m^{-1}}$ $\quad$ $k_B = 1.380\,650\,3 \times 10^{-23}\,\mathrm{J/K}$

$h = 6.626\,068\,8 \times 10^{-34}\,\mathrm{J/Hz}$ $\quad$ $R = 8.314\,472\,\mathrm{J\,K^{-1} mol^{-1}}$

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

To convert degrees Celsius to Kelvin, add 273.15.

Debye-Hückel formulae: $\ln \gamma_i = -A z_i^2 (\varepsilon T)^{-3/2} \sqrt{I_c}$
or $\ln \gamma_\pm = -A |z_+ z_-| (\varepsilon T)^{-3/2} \sqrt{I_c}$,
with $A = 1.107 \times 10^{-10}$.

Standard thermodynamic data at 298.15 K

Species	$\Delta_f H^\circ$ / $\mathrm{kJ\,mol^{-1}}$	$\Delta_f G^\circ$ / $\mathrm{kJ\,mol^{-1}}$	$C_{p,m}$ / $\mathrm{J\,K^{-1} mol^{-1}}$
$CO_{2(g)}$	−393.51	−394.37	37.1
$CO_{3(aq)}^{2-}$	−675.23	−527.90	
$CaCO_{3(s)}$	−1206.9	−1128.8	81.9
$CaO_{(s)}$	−634.92	−603.30	42.8