Chemistry 2740 Spring 2016 Final Examination

Time: 3 hours
Marks: 98
Aids allowed: calculator, 8.5×11-inch formula sheet
Useful data is given on the last page of the exam.
Instructions: 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).
Remember that a few short sentences go a long way to helping understand your work. Briefly note any procedures you carried out on your calculator (e.g. solving equations, linear regression, etc.).
If you use a graph to answer a question, make sure to provide a reasonable sketch of the graph, including properly labeled axes, as well as a brief explanation of what information the graph provides.

1 Answer all questions in this section.

Value of this section: 92

1. An EPR (electron paramagnetic resonance) spectrometer is used to study materials with unpaired electrons. In a magnetic field, the two possible spin orientations of the electron spin, aligned with the field and aligned against the field, have different energies, with the alignment of the spin with the field being energetically favored. The difference in energy between the two states is given by

$$\Delta\epsilon = g\beta B,$$

where the so-called g factor depends on the electron's environment, i.e. on the particular chemical species, $\beta = 9.2740 \times 10^{-24}\,\mathrm{J\,T^{-1}}$ is a constant known as the Bohr magneton, and B is the strength of the magnetic field in Tesla (T). The University of Lethbridge's EPR spectrometer uses an electromagnet that can generate a $1.45\,\mathrm{T}$ magnetic field. At $25\,^\circ\mathrm{C}$ for a compound with $g = 2.0142$, what is the probability that a paramagnetic molecule's unpaired spin is aligned with the field, i.e. that the spin is in the low-energy orientation? [6 marks]

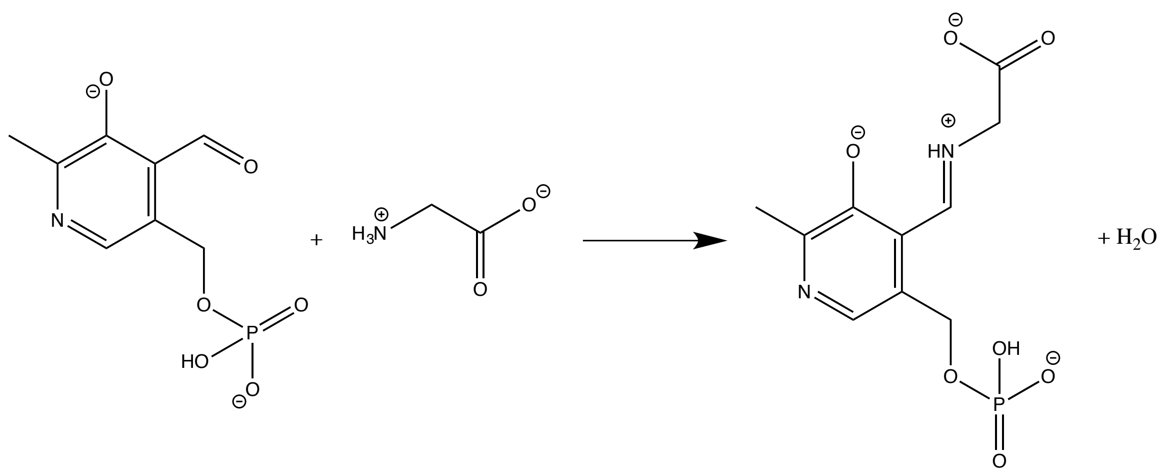
2. (a) Apples and other fruit produce ethene (C_2H_4), a gas that accelerates rotting. Plastic bags given to consumers for their produce in stores are impregnated with potassium permanganate ($KMnO_4$), which reacts with ethene to produce potassium hydroxide, MnO_2 and carbon dioxide. Balance this reaction, including all states of matter. [6 marks]

   (b) Calculate E° for this reaction. [5 marks]

(c) If the partial pressures of ethene and of carbon dioxide inside a plastic bag are, respectively, 10^{-4} bar and 3.9×10^{-4} bar, is the reaction thermodynamically allowed at 25 °C? [4 marks]

(d) 1 kg of apples kept in a cold room at 2 °C produces approximately 8×10^{-7} mol of ethene per hour. If potassium permanganate is placed in a container with 1 kg of apples in a cold room to help remove the ethene, at what rate is potassium permanganate used? [4 marks]

3. Pyridoxal-5'-phosphate (PLP),[1] the active form of vitamin B_6, reacts with amino acids to form Schiff bases. For example, here is the reaction of PLP with glycine:



Barannikov and coworkers have studied the thermodynamics of the reactions of PLP with several amino acids.[2] For the reaction of PLP with glycine, they calculated $\Delta_r H_m^{\circ\prime} = -2.2\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_r S_m^{\circ\prime} = 27.1\,\mathrm{J\,K^{-1}mol^{-1}}$ at pH 7.35 and an ionic strength of $0.656\,41\,\mathrm{mol\,L^{-1}}$. Fixing these conditions amounts to defining a new standard state with these properties.

(a) Calculate the equilibrium constant for this reaction under these conditions of pH and ionic strength at 37 °C. [4 marks]

(b) The conditions under which the measurements were carried out are near-physiological, although the ionic strength is perhaps a little high. Assume therefore that the enthalpy and entropy values given above are approximately those we would find inside a cell. If the glycine concentration in a human cell is about $4 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$, would there be more PLP or more Schiff base at equilibrium? [4 marks]

[1] If you're curious about the L in the abbreviation, it denotes the aldehyde form of this compound (pyridoxa*l*), which exists in equilibrium with a hydrate.

[2] V. P. Barannikov *et al.*, *Russ. J. Phys. Chem. A* **85**, 16 (2011).

4. The heat capacity of a bomb calorimeter (including the water it contains) was determined in the usual way and found to be $10.943\,\mathrm{kJ\,K^{-1}}$. When a $1.0428\,\mathrm{g}$ sample of the amino acid glycine ($C_2H_5O_2N$, molar mass $75.067\,\mathrm{g\,mol^{-1}}$) was ignited in the calorimeter by $10.1\,\mathrm{cm}$ of fuse wire ($\Delta_c u = -9.6\,\mathrm{J\,cm^{-1}}$), a temperature rise of $1.2402\,\mathrm{K}$ was observed. Calculate the standard enthalpy of formation of glycine. [10 marks]

   Note: The majority of the nitrogen in an organic compound burned in a bomb calorimeter is liberated as N_2.

5. Science-fiction movies sometimes depict gruesome consequences of low pressure on the human body when an astronaut ends up outside a space vessel or planetary habitat without a pressure suit. These consequences are often grossly exaggerated for visual effect, but it remains that a low ambient pressure does pose serious risks. One of the more serious risks is the evaporation (boiling) of the liquid coating the alveoli of the lungs. This is an aqueous solution containing a mixture of lipoproteins. For simplicity, we will treat this solution here as pure water. The atmospheric pressure on Mars is approximately $600\,\mathrm{Pa}$. What is the boiling point of water at this pressure? Compare your answer to the $37\,^\circ\mathrm{C}$ of the human body, and thus conclude whether the drying out of the aqueous solution lining the lungs is a danger for a person exposed to the Martian atmosphere unprotected. The vapor pressure of water at $25\,^\circ\mathrm{C}$ is $3167\,\mathrm{Pa}$. [10 marks]

6. Using Debye-Hückel theory, calculate the solubility of strontium chromate ($SrCrO_4$) in water at $25\,^\circ\mathrm{C}$ given that its K_{sp} at this temperature is 2×10^{-5}, and that the permittivity of water is $6.9390 \times 10^{-10}\,\mathrm{C^2J^{-1}m^{-1}}$. [10 marks]

7. The enzyme catalase catalyzes the decomposition of hydrogen peroxide to water and oxygen:

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

   Although catalase uses two equivalents of hydrogen peroxide, it behaves kinetically like an ordinary one-substrate enzyme. Ogura studied the kinetics of hydrogen peroxide decomposition catalyzed by horse liver catalase at pH 7 and $30\,^\circ\mathrm{C}$, and obtained the following data:[3]

$[H_2O_2]/\mathrm{mol\,L^{-1}}$	0.11	0.39	0.73	1.52	2.52	3.35	4.36
$v/\mathrm{mol\,L^{-1}s^{-1}}$	0.60	1.47	2.17	2.94	3.40	3.62	3.83

   The enzyme concentration in this experiment was $1.2 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$.

   (a) Determine K_M and k_{-2} (also known as k_{cat}). [9 marks]

   (b) Catalase has a very large turnover number (k_{-2}), much larger than k_{-1}. What is the value of k_1? [3 marks]

[3] Y. Ogura, *Arch. Biochem. Biophys.* **57**, 288 (1955). Only a subset of Ogura's data is given in order to save you a bit of work.

8. Prolactin is a hormone with a number of physiological functions, most famously stimulating milk production in mammalian females. The liver also has prolactin receptors, and binding of prolactin to these receptors has a number of effects on liver metabolism and endocrinology. Haro and Talamantes have studied the binding of prolactin to mouse hepatic (liver) receptors.[4] The reaction is reversible:

$$\mathrm{R} + \mathrm{P} \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} \mathrm{C},$$

with R representing the receptor, P the prolactin, and C the complex of R and P. They obtained the following data for the binding rate constant:

$T/\,^\circ\mathrm{C}$	37	30	23	8
$k_{+1}/10^4\,\mathrm{L\,mol^{-1}s^{-1}}$	12.6	8.1	7.1	2.3

(a) Using an Eyring plot, determine the enthalpy and entropy of activation. [8 marks]

(b) The reverse reaction (i.e. the elementary reaction associated with k_{-1}) has the following activation enthalpy and entropy:

$$\Delta^{\ddagger}_{-1}H_m = 40.9\,\mathrm{kJ\,mol^{-1}}$$
$$\Delta^{\ddagger}_{-1}S_m = -172\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

Determine the enthalpy and entropy of reaction. [6 marks]

(c) Sketch an entropy profile (i.e. entropy vs reaction coordinate) for this reaction. Clearly label the reactants, products and transition state. Your sketch should be drawn approximately to scale. [3 marks]

2 Answer *one* question in this section.

Value of this section: 6 marks

Extra answers will not be marked. If you attempt more than one question in this section, make it clear which one you want me to mark. Otherwise, I will mark the first one I see.

1. Describe some of the properties of ice cream that make it typical of the class of complex materials. [6 marks]

2. Describe the major parts of a bomb calorimeter, and explain briefly how this device works. [6 marks]

3. Discuss some of the ways in which enzymes are different from ordinary catalysts. [6 marks]

4. Starting from the second law of thermodynamics, prove that $\Delta G < 0$ for a thermodynamically allowed process at constant temperature and pressure. [6 marks]

[4] L. S. Haro and F. J. Talamantes, *Mol. Cell. Endocrinol.* **43**, 199 (1985).

Useful data

$F = 96\,485.342\,\mathrm{C\,mol^{-1}}$
$h = 6.626\,0688 \times 10^{-34}\,\mathrm{J/Hz}$
$k_B = 1.380\,6503 \times 10^{-23}\,\mathrm{J/K}$
$R = 8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}}$
To convert degrees Celsius to Kelvin, add 273.15.

$$\left.\begin{aligned} \ln\gamma_i &= -Az_i^2(\varepsilon T)^{-3/2}\sqrt{I_c} \\ \ln\gamma_\pm &= -A|z_+z_-|(\varepsilon T)^{-3/2}\sqrt{I_c} \end{aligned}\right\} \text{ with } A = 1.107 \times 10^{-10}$$

Standard thermodynamic data at 298.15 K		
Species	$\dfrac{\Delta_f H^\circ}{\mathrm{kJ\,mol^{-1}}}$	$\dfrac{\Delta_f G^\circ}{\mathrm{kJ\,mol^{-1}}}$
$C_2H_{4(g)}$	52.26	68.15
$CO_{2(g)}$	−393.51	−394.37
$H_2O_{(l)}$	−285.830	−237.140
$H_2O_{(g)}$	−241.826	−228.582
$KMnO_{4(s)}$	−813.4	−713.8
$KOH_{(s)}$	−424.764	−379.08
$MnO_{2(s)}$	−520.0	−465.2

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
1 H 1.01																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg							

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Have a great summer!