Chemistry 2740 Spring 2021 Final Examination

Total marks: 95

Submission: From the time you open the test in Crowdmark, you have a total of $3\frac{1}{2}$ **hours** (210 minutes) to complete the test **and upload your answers to Crowdmark**.

General instructions: Under no circumstances are you to discuss the contents of this test with, or obtain assistance from, any person by any means prior to the submission deadline of **11:59 p.m. Saturday, April 17th**. You may however email me to clear up minor issues you run into while doing the test. Note that I can't watch my email every minute of the day, so questions sent at the last minute or late at night may not receive timely answers.

You can use any resources you like (textbook, web resources, etc.), and any computational tools (calculator, spreadsheet, etc.). However, the point of this test is to evaluate your understanding of the material so you must give full details of any work or reasoning. **Answers without detailed work will receive NO credit.**

Keep in mind the **firm** deadlines: $3\frac{1}{2}$ **hours, ending before 11:59 p.m. April 17th.**

Choice: In sections 2 and 3, answer only the required number of questions. Make sure it is clear in your submitted work which question you are answering. Do not submit answers to more questions than required. I will only grade the required number of answers.

Graphs: If you need a graph to answer a question, you must show your graph. Given the nature of this test, you can (a) hand-sketch your graph, or (b) generate an image of your graph from (e.g.) a spreadsheet. An acceptable graph will have fully labeled axes. Additionally, the line of best fit must be shown with the data.

Solving equations: If you use a calculator's solver or a computer program (e.g. Excel) to solve an equation, make sure to give me full details of the solution: the equation solved, the initial guess, and any constraints placed on the solution.

Thermodynamic data

Species	$\frac{\Delta_f H^\circ}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta_f G^\circ}{\mathrm{kJ\,mol^{-1}}}$	$\frac{S_m^\circ}{\mathrm{J\,K^{-1}mol^{-1}}}$
$Cd^{2+}_{(aq)}$	−72.38	−77.74	−61.1
$Hg_2SO_{4(s)}$	−743.4	−626.1	200.5
$P_{2(g)}$	143.65		218.07
$P_{4(g)}$	58.91		279.93
$SO^{2-}_{4(aq)}$	−909.34	−744.00	
$Si_{(s)}$	0	0	18.0

1 Answer all questions in this section.

Value of questions in this section: 71

1. In vertebrates, retinoic acid ($C_{19}H_{27}COOH$) plays an important role in specifying the position along the anterior-posterior axis. The final step in the biosynthesis of retinoic acid is the oxidation of retinal ($C_{19}H_{27}CHO$). Different oxidizing agents can be used, including oxygen. If oxygen is the oxidizing agent, the reaction makes hydrogen peroxide (H_2O_2) in addition to retinoic acid. The cellular medium is nearly neutral in pH. Balance this reaction. **5 marks**

2. The enzyme Hmp catalyzes the oxidation of nitric oxide to nitrate in many bacteria. One of the steps in the catalytic mechanism is the binding of an $\mathrm{Hmp \cdot NADH \cdot O_2}$ complex to NO. This step has a large rate constant: $2.4 \times 10^9\,\mathrm{L\,mol^{-1}s^{-1}}$ at 37 °C.[1] Nitric oxide has a bond length of 106 pm (which gives a rough radius for the molecule) and a diffusion coefficient in water of $3.0 \times 10^{-9}\,\mathrm{m^2/s}$ at 37 °C.[2] The radius of Hmp is about 3.6 nm;[3] for lack of data to the contrary, you can assume that the complex of Hmp with NADH and oxygen is similar. The viscosity of water at this temperature is 0.698 mPa s. Is the binding of NO to Hmp diffusion-controlled? **6 marks**

3. The rate constants for the binding and dissociation of acetylcholine (ACh) to an acetylcholine binding protein (AChBP), **6 marks**

$$\mathrm{ACh + AChBP \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C},$$

have been measured at 25 °C. These rate constants were found to have the values[4] $k_1 = 1.1 \times 10^8\,\mathrm{L\,mol^{-1}s^{-1}}$ and $k_{-1} = 120\,\mathrm{s^{-1}}$. What is the empirical equilibrium constant for this reaction? Assuming ideal behavior, how would this empirical equilibrium constant relate to the thermodynamic equilibrium constant?

4. Phosphorus-32 is a radioactive isotope frequently used to label biomolecules in biochemical experiments. It has a half-life of 14.265 d. **11 marks**

   (a) Radioactively labeled compounds are sold on an activity basis. For example, you can buy a vial that contains 9.25 MBq of ^{32}P-labeled GTP (i.e. enough labeled GTP such that the material in the vial emits 9.25 MBq of radioactivity) for about $1000. How many moles of ^{32}P-labeled GTP does the vial contain? [7 marks]

   Note: 1 Bq = 1 decay per second.

   (b) Suppose that $\frac{2}{3}$ of a fresh 9.25 MBq bottle of ^{32}P-labeled GTP was used in some experiments soon after arriving in the lab. How long can the rest of the bottle be

[1] A. M. Gardner et al., *J. Biol. Chem.* **275**, 12581 (2000)
[2] I. Zacharia and W. M. Deen, *Ann. Biomed. Eng.* **33**, 214 (2005)
[3] A. Ilari et al., *J. Biol. Chem.* **277**, 23725 (2002)
[4] S. B. Hansen et al., *J. Biol. Chem.* **277**, 41299 (2002)

kept if we want to be able to do another set of experiments that will require 30 measurements, each of which will use 0.02 MBq of ^{32}P-labeled GTP? [4 marks]

5. From 1911 to 1990, the Weston cell was used as the standard for emf measurements because it produces a highly stable voltage. The cell diagram of a Weston cell (slightly simplified) is **14 marks**

$$Cd_{(s)}|CdSO_{4(aq)}|Hg_2SO_{4(s)}|Hg_{(l)}.$$

The mercury separates from the solution. Cadmium(II) sulfate has a negligible solubility in mercury. The reactions at the anode and cathode are, respectively,

Anode: $Cd_{(s)} \longrightarrow Cd^{2+}_{(aq)} + 2\,e^-$

Cathode: $Hg_2SO_{4(s)} + 2\,e^- \longrightarrow 2\,Hg_{(l)} + SO^{2-}_{4(aq)}$

Using Debye-Hückel theory, calculate the emf generated by a Weston cell at 25 °C if the concentration of cadmium sulfate is 0.0045 mol L^{-1}.

6. A protease (an enzyme that cuts up proteins) discovered in *Moringa oleifera*[5] seeds was tested for its ability to degrade casein. The following initial rate data were obtained:[6] **7 marks**

[casein]/g L^{-1}	v/U min^{-1}
0.12	6.0
0.26	13.7
0.50	20.6
1.00	31.2
2.01	39.6
4.01	49.5
5.98	56.1
8.00	60.0
10.00	61.1

(U is an arbitrary unit used as a measure of enzyme activity when there is no easy way to quantify the amount of substrate that has reacted. In this case, U is based on the increase in optical density of the solution at 280 nm.)

Determine v_{max} and the Michaelis constant of this enzyme in this preparation.[7]

[5] *M. oleifera* is a fast-growing tree native to India.
[6] X. Wang et al., *Int. J. Biol. Macromol.* **171**, 539 (2021)
[7] v_{max} depends on the amount of enzyme used, which was not determined in this experiment.

7. The rate constant for the dissociation of carbon monoxide from myoglobin has been measured as a function of temperature in aqueous solution.[8] The following is a selection of points from the original data set (which was very large): **12 marks**

T/K	274	282	292	303	325	342
k/s^{-1}	5.01×10^{-3}	1.73×10^{-2}	3.41×10^{-2}	9.51×10^{-2}	8.40×10^{-1}	4.30×10^{0}

(a) Calculate the standard enthalpy and entropy of activation for this reaction. [10 marks]

(b) Interpret the entropy of activation. What can we learn from the size and sign of this quantity? [2 marks]

8. The reaction of nitric oxide (NO) with an oxygen-containing species such as O_2 or O_3 in the gas phase is chemiluminescent: photons are produced as a byproduct of the reaction. For example, the reaction **10 marks**

$$\mathrm{NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}},$$

produces light in the red to infrared range. The mechanism of this reaction is thought to be the following:

$$\mathrm{NO + O_3 \xrightarrow{k_1} NO_2{}^* + O_2} \tag{1a}$$

$$\mathrm{NO_2{}^* \xrightarrow{k_2} NO_2} + h\nu \tag{1b}$$

$$\mathrm{NO_2{}^* + M \xrightarrow{k_3} NO_2 + M} \tag{1c}$$

In these reactions, $NO_2{}^*$ represents an NO_2 molecule carrying excess energy. There are two ways for the energized NO_2 molecule to shed this excess energy:

(i) It can simply radiate the energy away in the form of a photon [represented by $h\nu$ in reaction (1b)].

(ii) Alternatively, an energized NO_2 molecule can collide with another molecule (M), transferring its excess energy to the collision partner in the process [reaction (1c)].

The intensity of the luminescence (I, the number of photons produced per unit time) is proportional to the rate of reaction (1b).

(a) Derive a rate law for the rate of production (I) of photons given that reactions (1b) and (1c) are fast. [8 marks]

(b) To what does the rate law simplify if [M] is very large? [2 marks]

Bonus: The quantum yield is the fraction of energizing events that lead to the production of a photon. Derive an equation for the quantum yield. [2 marks]

[8] M. Filiaci and G. U. Nienhaus, *Eur. Biophys. J.* **26**, 209 (1997)

2 Answer *one* question in this section

Value of this section: 8 marks

1. (a) A typical laboratory gas cylinder has a storage volume of 29.5 L and will be filled by the supplier to a pressure of 14 MPa. Calculate the reversible work required to fill such a cylinder isothermally at room temperature (20 °C) using nitrogen initially stored at 90 kPa (normal atmospheric pressure in Lethbridge). [7 marks] **8 marks**

   (b) How does the reversible work relate to the work that must be done in a real process? [1 mark]

2. The molar heat capacity of solid silicon is well described by the equation[9] **8 marks**

$$C_{p,m} = 23.698 + 3.305 \times 10^{-3}T - \frac{4.354 \times 10^5}{T^2}.$$

   In this equation, $C_{p,m}$ is in $\mathrm{J\,K^{-1}mol^{-1}}$ and T is in Kelvin. Calculate the molar entropy of silicon at 150 °C.

3 Answer *two* questions in this section.

Value of this section: 16 marks

1. Phosphorus boils at 553.7 K. In the gas phase, there is an equilibrium between P_2 and P_4 molecules. Calculate the equilibrium constant for the conversion of P_4 to P_2 at the boiling point of phosphorus. **8 marks**

2. (a) The vapor pressure of a $0.900\,\mathrm{mol\,kg^{-1}}$ solution of potassium chloride in water (mol KCl per kg water) at 25 °C is 23.09 torr.[10] What is the activity of water in this solution? [2 marks] **8 marks**

   (b) We normally treat the autoionization of water using the equation $K_w = (a_{\mathrm{H}^+})(a_{\mathrm{OH}^-})$. However, this equation involves an approximation. What is it? [2 marks]

   (c) What is the pH of the neutral solution described in part a? Give your answer to two decimal places. [4 marks]

3. The equilibrium constant for the reaction **8 marks**

$$C_6H_{6(g)} + 3\,H_{2(g)} \rightleftharpoons C_6H_{12(g)}$$

   is 3.17×10^{-2} at 600 K. If we start out with 4.3 bar of benzene and 8.2 bar of hydrogen, what are the equilibrium pressures of all the gases?

[9] Glasov and Pashinkin, *High Temp.* **39**, 413 (2001)
[10] H. N. Parton, *Trans. Faraday Soc.* **33**, 617, 1937