Chemistry 2740 Spring 2020 Final Examination

Due: 8:00 p.m. Thursday, April 9. Submit through Crowdmark (accessed from Moodle). Late submissions will not be accepted. The exam is intended to take roughly three hours of your time (with the appropriate multiple for students with time accommodations). Allocate an appropriate amount of time to do this exam during the 32-hour period allowed, keeping in mind that you will need some time to scan/photograph and upload your answers.

Marks: 98

Useful data:

Standard reduction potentials at 298.15 K	
Reduction process	$E°/\text{V}$
$\text{AuCl}^-_{4(\text{aq})} + 3\text{e}^- \rightarrow \text{Au}_{(\text{s})} + 4\text{Cl}^-_{(\text{aq})}$	+0.93

Use the data tables in the book for any constants or other data not provided above. **Do not use any other sources of data.**

Instructions: Under no conditions are you to discuss the contents of this test with any person by any means prior to the submission deadline of 8:00 p.m. Thursday, April 9.

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.**

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. However, an acceptable graph will have fully labeled axes (so don't just take a picture of your calculator screen). The line of best fit must be shown with the data.

Any non-trivial use of a calculator or other computational device must be described. For example, if you use a calculator to solve a nonlinear equation, you need to make it clear what equation was solved, and provide any other inputs you used to the calculation.

Ideally, you would start each question on a new page. You can submit multiple pages per question, if necessary. For questions with parts, you do *not* need to start a new page for each part.

1. One method often suggested for reducing our excessive carbon dioxide emissions is to replace inefficient appliances by more efficient models. One potential problem with this is that there is an energy cost to manufacturing an appliance, so it is not always clear if it is better to keep an existing appliance as long as possible, or whether there would be a reasonably rapid recovery of the energy invested in making the appliance through improved energy efficiency of a newer model. **6 marks**

   Manufacturing a coffee maker uses an average of 184 MJ of energy.[1] A rough estimate of the energy used in shipping adds another 3 MJ to the total energy required to make the coffee maker and bring it to your local store, assuming that the coffee maker is produced in Asia and mostly transported by ship and by rail. (Shipping in bulk is surprisingly energy efficient.)

   An older drip filter coffee maker uses an average of 125 kWh per year.[2] A newer model with all the latest energy-saving features might reduce the energy used by 20%. (All of these figures depend greatly on the amount of coffee you make, how long you leave the machine in "keep warm" mode, etc.) A typical lifetime for a coffee maker is six years. Would replacing an older coffee maker that is still working with a newer model result in net energy savings over the expected six-year lifespan of the new coffee maker?

   Hint: You need to convert kWh to the SI unit of energy. What is the relationship between a joule and a watt? Note: You must show how you carried out the unit conversion for full marks.

2. The Boudouard reaction is the following: **11 marks**

$$2\,\mathrm{CO_{(g)}} \rightleftharpoons \mathrm{CO}_{2(g)} + \mathrm{C_{(s)}}$$

   In industrial processes involving carbon monoxide, this reaction can be a serious nuisance since graphite deposited in gas lines can eventually block them.

   (a) Calculate the equilibrium constant for this reaction at 298.15 K. [4 marks]

   (b) The equilibrium constant $K = 1$ at 975 K. Using your answer to part a and this additional piece of data, estimate the enthalpy of reaction. [4 marks]

   (c) Using the thermodynamic data provided in the textbook, calculate the enthalpy of reaction. Does this value agree with your answer from part b? [3 marks]

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[1] N. Duque Ciceri, T. G. Gutowski and M. Garetti, A tool to estimate materials and manufacturing energy for a product, *Proceedings of the 2010 IEEE International Symposium on Sustainable Systems and Technology*

[2] ENERGY STAR Market & Industry Scoping Report: Coffee Makers (2011)

3. The heat capacity of solid fluorobenzene (in $\mathrm{J\,K^{-1}mol^{-1}}$) is well fit by the equation **10 marks**

$$C_p = c_3T^3 + c_4T^4 + c_5T^5$$

over the temperature range 0–35 K, where T is in Kelvin and

$$c_3 = 4.026 \times 10^{-3},$$
$$c_4 = -1.67 \times 10^{-4},$$
$$c_5 = 1.997 \times 10^{-6}.$$

(a) Calculate the heat required to warm solid fluorobenzene from 0 to 35 K. [5 marks]

(b) Calculate the entropy change in warming solid fluorobenzene from 0 to 35 K. [5 marks]

4. Methyl phosphate hydrolyzes spontaneously in aqueous solution at high temperatures: **20 marks**

$$\mathrm{CH_3OPO^{2-}_{3(aq)} + H_2O_{(l)} \xrightarrow{k} CH_3OH_{(aq)} + HOPO^{2-}_{3(aq)}}$$

In a classic study, Wolfenden, Ridgway and Young studied this reaction at pH 10 and obtained the following data:[3]

T/K	$k_{\mathrm{obs}}/\mathrm{s^{-1}}$	$[\mathrm{H_2O}]/\mathrm{mol\,L^{-1}}$
392	2.3×10^{-7}	52.4
392	1.2×10^{-7}	52.4
411	1.4×10^{-6}	51.5
434	1.6×10^{-5}	50.3
444	4.4×10^{-5}	49.7
461	2.4×10^{-4}	48.7
474	5.8×10^{-4}	48.1

(a) k_{obs} is an "observed rate constant" related to the true second-order rate constant by $k_{\mathrm{obs}} = k[\mathrm{H_2O}]$. Why were they only able to measure this observed rate constant? [2 marks]

(b) To put the observed rate constants into perspective, what is the half-life at 411 K? Express your answer in common time units (seconds, minutes, hours, ...) such that the magnitude or your answer is easily grasped. [3 marks]

(c) Calculate the second-order rate constant at each temperature. Then, determine the enthalpy and entropy of activation for this reaction. [13 marks]

(d) Interpret the entropy of activation. What does it tell us about this reaction? [2 marks]

[3] Selected kinetic data from R. Wolfenden, C. Ridgway and G. Young, *J. Am. Chem. Soc.* **120**, 833 (1998). The repeated measurements at 392 K are not an error. Mole density of water estimated from data in the *CRC Handbook of Chemistry and Physics*, 100th edition.

5. The dihydrogen phosphate ion ($H_2PO_4^-$) has a K_a at 25 °C of 6.3×10^{-8}. (The acidity of the remaining proton is negligible in this question.) Using Debye-Hückel theory, calculate the pH of a 0.0053 mol/L solution of sodium dihydrogen phosphate in water. Report your pH to two decimal places. **16 marks**

   Hint: The ionic strength can be calculated immediately. Why?

6. (a) Solid gold nanoparticles can be made by reducing the tetrachloroaurate(III) ion ($AuCl_4^-$) in aqueous solution. A possible reducing agent would be methanol, which oxidizes to formaldehyde (CH_2O). Write a balanced reaction for this process in neutral solution. [4 marks] **18 marks**

   (b) Would you expect to make gold nanoparticles if $[AuCl_4^-] = 0.13\,\text{mol}\,\text{L}^{-1}$, $[Cl^-] = 0.0041\,\text{mol}\,\text{L}^{-1}$, $[CH_2O] = 1.2\,\text{mol}\,\text{L}^{-1}$, $[CH_3OH] = 0.032\,\text{mol}\,\text{L}^{-1}$, and the pH is 7.0 at 25 °C? $E°$ for the reduction of formaldehyde to methanol is −0.70 V. Ignore non-ideal behavior. [6 marks]

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

   Hint: Don't use the reaction above, for which it is difficult to find the needed data. Instead, couple the tetrachloroaurate(III) half-reaction to the H^+/H_2 half-reaction and work from there.

7. $Ru(CO)_5$ is unstable in solution, converting to $Ru_3(CO)_{12}$. The mechanism is thought to be **17 marks**

$$Ru(CO)_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru(CO)_4 + CO$$

$$Ru(CO)_4 + Ru(CO)_5 \xrightarrow{k_2} Ru_2(CO)_9$$

$$Ru_2(CO)_9 + Ru(CO)_5 \xrightarrow{k_3} Ru_3(CO)_{12} + 2\,CO$$

   Steps 2 and 3 are thought to be fast.

   (a) Derive a rate law for this reaction. [14 marks]

   (b) Under typical experimental conditions, [CO] is relatively small. What rate law do we obtain in this case? Is it a simple rate law? If so, what is the order of reaction with respect to each reactant or product appearing in the rate law? [3 marks]

A final note: As these are strange times, I hesitate to wish you a "great summer" as I would normally do at this point. It's going to be a weird summer for most of us. I will instead just wish you well. I hope that you and your loved ones stay safe. And I hope we can all see each other on campus again this fall.