Chemistry 2740 Spring 2021 Test 3

Total marks: 38

Submission: From the time you open the test in Crowdmark, you have a total of **2 hours** to complete the test **and upload your answers to Crowdmark**.

General instructions: Under no conditions 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 **7:00 p.m. Friday, March 26th**. 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 last-minute questions 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 <u>NO</u> credit.**

Make sure to use a sufficiently dark pencil or pen so that your work will scan or photograph well. Also, verify the quality of your images before uploading them. If I can't read it, I can't mark it. Color is permitted if you think it would be useful. While the test is intended to be hand-written—neatly please!—I don't mind computer (word processor, spreadsheet) output if you think it's helpful for some problems.

Keep in mind the **firm** deadlines: **two hours, ending before 7:00 p.m.**

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

1. The oxidation of glutathione by a diruthenium complex in acidic solution has the following stoichiometry: **14 marks**

$$Ru_2O^{4+} + 2\,GSH \longrightarrow 2\,[Ru(bipy)_2(OH_2)_2^{2+}] + GSSG + H_2O,$$

where GSH is glutathione, GSSG is glutathione disulfide, and Ru_2O^{4+} is an abbreviation for the transition-metal complex

$$[(bipy)_2(OH_2)RuORu(OH_2)(bipy)_2]^{4+}.$$

This reaction was studied in solutions containing a large excess of both acid and glutathione relative to the diruthenium complex.[1] Under these conditions, the reaction displays first-order kinetics with respect to Ru_2O^{4+}. The following first-order rate constants were observed at different GSH and H^+ concentrations (always in large excess over Ru_2O^{4+}) at 25.5 °C:

Experiment	$[GSH]/10^{-3}\,mol\,L^{-1}$	$[H^+]/mol\,L^{-1}$	$k_{obs}/10^{-4}s^{-1}$
1	0.20	0.01	0.75
2	0.80	0.01	2.91
3	2.00	0.01	7.28
4	0.80	0.02	1.50
5	0.80	0.04	0.72

(a) Determine the rate law for this reaction. Explain your reasoning. [6 marks]

(b) Obtain the value of the rate constant appearing in your rate law. This may involve repetitive calculations. Feel free to use a spreadsheet after showing one sample calculation. [8 marks]

2. The following table gives the cumulative number of Covid-19 cases in Lethbridge up to each of the given dates: **10 marks**

Date	March 15	March 16	March 17	March 18	March 19
N	2586	2622	2656	2676	2720

Estimates of the mean period of time during which a person is infectious vary quite a bit. However, a recent estimate by the Australian Covid-19 National Incident Room Surveillance Team places the duration of this period at 16 days.[2] Estimate the effective reproduction number for Lethbridge during this period. In a few words, what does this number tell us?

[1] G. A. Ayoko, J. F. Iyun and A. T. Ekubo, *Transition Met. Chem.* **18**, 6 (1993).

[2] COVID-19 National Incident Room Surveillance Team, *Commun. Dis. Intell.* **45** (2021), DOI: 10.33321/cdi.2021.45.2

3. One method for removing arsenic-based complex ions from solution involves passing the solution over a metal. The mechanism is complex, but the net result is that the complex ions are adsorbed onto the surface. Strangely, depending on the metal and possibly on other factors, one can observe either first-order or second-order kinetics. In one set of experiments,[3] sodium hydrogen arsenate solutions were incubated with zinc metal, and the arsenate concentration in solution was measured as a function of time: **14 marks**

t/min	0.0	29.9	59.9	90.1	150.0	180.3	209.9	240.1
c/mg L^{-1}	50.0	43.1	36.5	32.5	23.1	22.3	20.9	20.8

Note: the concentrations are given as mg of arsenic per liter.

(a) Do the data fit a first-order or a second-order rate law better? [10 marks]

Note: These are real data, so they are imperfect and some judgment will have to be applied.

(b) What is the rate constant (for the rate law you judge to be the better one)? [2 marks]

(c) Health Canada's guidelines suggest that arsenic in drinking water should be limited to 0.010 mg L^{-1}. Arsenic levels in Alberta waterways are sometimes much higher than this due to local geology, seasonal changes in water flow, etc. Suppose that we wanted to treat drinking water with zinc under conditions identical to those of the study described above, and that the water we were treating had an initial arsenic concentration of 0.035 mg L^{-1}. How long would it take for the arsenic concentration to fall to the recommended maximum of 0.010 mg L^{-1}? [2 marks]

[3] M. Rajendran and D. Thangavelu, *J. Hazard. Mater.* **409**, 124564 (2021)