Chemistry 2740 Spring 2022 Test 3

Total marks: 45

Submission: From the time you open the test in Crowdmark, you have a total of **75 minutes** 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 while the test is open. You may however email me to clear up minor issues you run into while doing the test.

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.**

Please only use data on this test paper and in the textbook. **Do not** use data obtained from other sources as this might cause your answers to differ from mine.

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 I'm not very fussy about significant figures—that's Wayne's job—I am picky about a couple of things:

- You should give answers to a reasonable number of decimal places given the input data. Don't give me answers to eight decimal places if the data aren't that accurate, and don't round your final answer so much that I can't tell if it's right or wrong. Use reasonable judgment. Of course, you can't go wrong following the significant figure rules.
- All the digits in your final answer should be correct, which generally means that you should store intermediate results in calculator memories. Alternatively, keep a few extra digits in intermediate steps.

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. Short questions **13 marks**

   (a) Suppose that, for a reaction with stoichiometry A $\rightarrow$ 2B and with an initial concentration of A of $0.32\,\mathrm{mol\,L^{-1}}$, $4.32 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ of B accumulates in the first 32 s. What is the rate of reaction? [4 marks]

   (b) The half-life is used much more often in connection with first-order reactions than for any other order of reaction. Why? [2 marks]

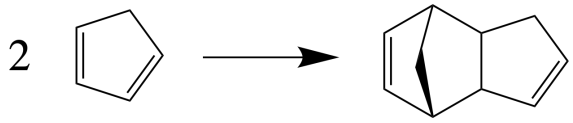
   (c) Suppose that the following are elementary reactions:

$$\mathrm{X_{2(aq)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,X_{(aq)}}$$

$$\mathrm{X_{(aq)} + Y_{(aq)} \xrightarrow{k_2} XY_{(aq)}}$$

   Write the mass-action rate equation for [X]. [3 marks]

   (d) Cyclopentadiene dimerizes to dicyclopentadiene in a second-order reaction:



   The rate constant for this reaction in toluene at 120 °C is $6.13 \times 10^{-2}\,\mathrm{L\,mol^{-1}s^{-1}}$. If a solution with an initial concentration of cyclopentadiene of $0.53\,\mathrm{mol\,L^{-1}}$ is held at 120 °C, how long would it take for 20% of the cyclopentadiene to be converted to dicyclopentadiene? [4 marks]

2. For the reaction **12 marks**

$$\mathrm{2\,HgCl_{2(aq)} + C_2O_{4(aq)}^{2-} \longrightarrow Hg_2Cl_{2(s)} + 2\,Cl_{(aq)}^{-} + 2\,CO_{2(g)}}$$

   the following initial rate data were obtained:

Experiment	$[\mathrm{HgCl_2}]/\mathrm{mol\,L^{-1}}$	$[\mathrm{C_2O_4^{2-}}]/\mathrm{mol\,L^{-1}}$	$v/10^{-7}\mathrm{mol\,L^{-1}s^{-1}}$
1	0.096	0.13	2.1
2	0.096	0.21	5.5
3	0.171	0.21	9.8

   (a) Determine the rate law and rate constant. [10 marks]

   (b) Do you think this is an elementary reaction? Why or why not? Use the strongest evidence available to decide this question. [2 marks]

3. Because rocks naturally contain some radioactive elements, concrete, which is a mixture of cement and rocky material, is somewhat radioactive. (So is just about everything else, so don't panic.) The specific radioactivity is measured in $\mathrm{Bq\,kg^{-1}}$ (Bq per kilogram of concrete), and the contributions of different isotopes can be separated. (Recall that a Bq is one decay per second.) The radioactivity will depend on the source of the rocks used to make it. Suppose that a particular batch of concrete has a ^{226}Ra activity of $35.8\,\mathrm{Bq\,kg^{-1}}$. Given that the half-life of ^{226}Ra is 1600 y, what is the concentration of radium in the concrete in units of $\mathrm{mol\,kg^{-1}}$? **8 marks**

4. We will see later that gas-phase unimolecular reactions can display either (a) a first-order rate law, (b) a second-order rate law, or (c) a complex rate law, depending on the experimental conditions. Vlasov and coworkers have studied the thermal decay of nitromethane (NM) and obtained the following data in one particular experiment at 1394 K:[1] **12 marks**

t/μs	0	4.75	14.99	21.19	29.04	37.52
$[\mathrm{NM}]/10^{-8}\mathrm{mol\,cm^{-3}}$	1.043	0.745	0.420	0.235	0.129	0.088

Determine whether the data obey a first- or second-order rate law, or neither. Explain how you came to your decision. In the event that you think a first- or second-order rate law is a good fit, calculate the rate constant.

[1] P. A. Vlasov, N. M. Kuznetsov, Yu. P. Petrov and S. V. Turetskii, *Kinet. Catal.* **59**, 6 (2018).