Chemistry 2740 Spring 2022 Test 4

Total marks: 21 marks

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.

1. Acetylcholine (ACh) is a critical neurotransmitter in animals. Cobra venom contains a compound called α-cobratoxin (αCT) that acts by binding to the receptor that acetylcholine binds to during nerve-muscle communication, thus blocking this communication and paralyzing the animal. In the fresh water snail, a related protein, acetylcholine binding protein (AChBP), also binds to acetylcholine, but acts as a regulator of acetylcholine activity rather than as a receptor. Despite this difference in function, AChBP is a good model for the binding of various substances to the acetylcholine receptor. Consider the following two binding reactions of snail AChBP:[1] **8 marks**

$$\text{AChBP} + \text{ACh} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{AchBP} \cdot \text{ACh}$$

$$\text{AChBP} + \alpha\text{CT} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{AchBP} \cdot \alpha\text{CT}$$

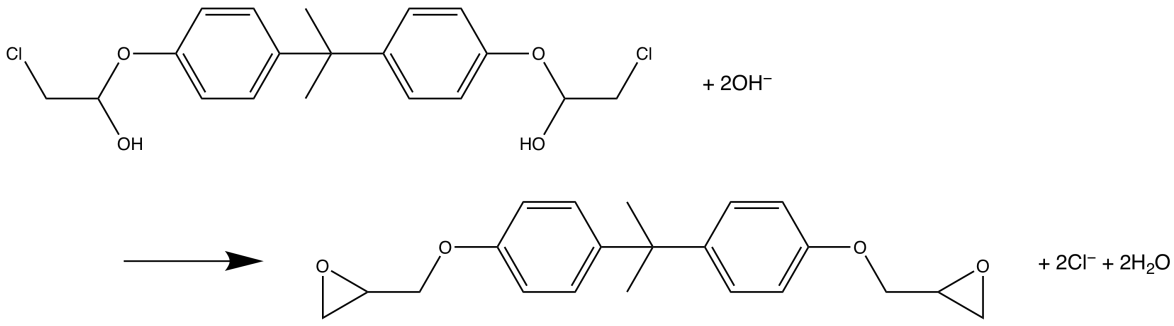
$k_1/\text{L mol}^{-1}\text{s}^{-1}$	k_{-1}/s^{-1}	$k_2/\text{L mol}^{-1}\text{s}^{-1}$	k_{-2}/s^{-1}
1.1×10^8	120	3.3×10^6	0.011

Calculate the equilibrium constant for the reaction

$$\text{AchBP} \cdot \text{ACh} + \alpha\text{CT} \rightleftharpoons \text{AchBP} \cdot \alpha\text{CT} + \text{ACh}$$

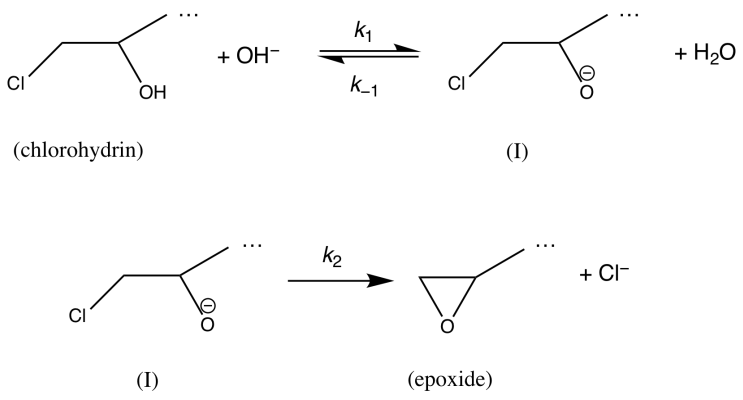
and comment on the implication of this calculation for the toxicity of cobra venom in snails (and, by extension, in other animals with acetylcholine receptors).

2. The following is an important reaction in the industrial production of bisphenol A expoxy resins: **13 marks**



Note that the reactants and products are symmetric and that the same reaction occurs at both ends of the molecule. We can therefore focus on the chlorohydrin functionality that is converted to an epoxide in this reaction. The reaction mechanism is thought to be[2]

[1] Data from S. B. Hansen et al., *J. Biol. Chem.* **277**, 41299 (2002).
[2] M. N. Makhin and M. S. Klebanov, *Kinet. Catal.* **61**, 238 (2020)



The reaction is usually carried out in an organic solvent. Water is in great excess, but the concentration of water in the mixture can be changed from experiment to experiment.

(a) Derive a rate law for this mechanism assuming that the intermediate I is highly reactive. [10 marks]

(b) If we assume that the concentration of water is constant,[3] the rate law in any given experiment will appear to be a simple rate law. What is this simple rate law and what is the apparent rate constant? [3 marks]

Bonus: The authors of this study obtained the apparent rate constant as a function of the water concentration at 60 °C.

$[H_2O]/\text{mol L}^{-1}$	0.14	0.32	0.54	1.20
$k_{\text{app}}/\text{L mol}^{-1}\text{s}^{-1}$	622	385	271	51

As usual in physical chemistry, we would like to transform the equation relating the apparent rate constant to the concentration of water to a form that will give us a linear graph. Find this transformation, then generate the appropriate graph and verify whether their data fit your theoretical expression. [4 marks]

[3] Water is only slightly soluble in the solvent used, methyl isobutyl ketone. Accordingly, if the solvent starts out being saturated with water, any water produced by the reaction will separate out and sink to the bottom of the reaction vessel since water is denser than the ketone. This keeps the concentration of water in the organic phase constant throughout the reaction.