Chemistry 2740 Spring 2022 Assignment 2

Due: Thursday, May 5 at noon

Assignments submitted after that time will not be accepted unless there are extenuating circumstances.

Total marks: 24

Fry and coworkers have studied the hydrolysis of tetracholoaurate(III) in aqueous solution, from which they obtained the apparent first-order rate constant for the following elementary reaction:¹

$$AuCl_{4(aq)}^{-} + H_2O_{(l)} \longrightarrow AuCl_3(OH_2)_{(aq)} + Cl_{(aq)}^{-}$$

- 1. Why is the first-order rate constant only an "apparent" rate constant? How does the apparent rate constant relate to the elementary rate constant? [4 marks]
- 2. The measured rate constants were as follows:

$$T/^{\circ}$$
C | 10.0 | 15.3 | 20.0 | 26.0 | 34.5 | $k_{\rm app}/10^{-2}{\rm s}^{-1}$ | 0.40 | 0.60 | 0.97 | 1.55 | 3.10

Calculate the elementary rate constant at each temperature for this reaction. [4 marks]

- 3. Determine the entropy and enthalpy of activation. [14 marks]
- 4. What does the entropy of activation tell us about the nature of the transition state? [2 marks]

Data: Mole density (c_w) of water

$$T/^{\circ}$$
C 10.0 15.3 20.0 26.0 34.5 $c_w/\text{mol L}^{-1}$ 55.45 55.42 55.39 55.31 55.16

¹F. H. Fry et al., *Inorg. Chem.* **5**, 1943 (1966)