Experiment 12H, Parts A and B

AHRM 8/17

PRINCIPLES OF EQUILIBRIUM AND THERMODYNAMICS

MATERIALS: 0.0200 M $Fe(NO_3)_3$ in 1 M HNO_3, 0.000200 M KSCN, 2.0 M HNO_3, solid $Fe(NO_3)_3 \cdot 9H_2O$ with accompanying spatula, solid KSCN, Spectronic-200, cuvettes, test tubes, 50-mL beakers, small plastic weighing dish

PURPOSE: The purpose of this experiment is to determine the equilibrium constant K for a chemical reaction and illustrate LeChatelier's Principle.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Select an appropriate wavelength for use in experiments involving absorbance of light.
2. Evaluate experimental data to obtain the equilibrium constant K.
3. Interpret the measurable effects of disturbances to a system at equilibrium in terms of LeChatelier's Principle.

PRE-LAB: Complete the Pre-Lab Assignment at the end of this document **before** going to lab. You will need some of the answers to these questions in order to get started with the experiment.

DISCUSSION:

A Complex Ion Formation Reaction. Choosing a chemical reaction that easily illustrates the important principles of equilibrium and thermodynamics is difficult. One reaction most commonly chosen for this purpose is the subject of this experiment. It is an example of a class of reactions known as complex ion formation reactions. Specifically, it is the reaction

$$Fe^{3+}(aq) + SCN^-(aq) \leftrightarrows FeSCN^{2+}(aq) \qquad (1)$$

Associated with this reaction is an equilibrium constant K, which varies with temperature depending on the exo- or endo-thermicity of the reaction. The product of this reaction is a complex ion, $FeSCN^{2+}$, which very intensely absorbs certain wavelengths of visible light. The other species, under the conditions of this experiment, absorb little if any visible light. (Normally, solutions of Fe^{3+} have a yellow color, but when dissolved in nitric acid, this color disappears.) Hence, solutions in which this reaction is occurring will appear colored due solely to the concentration of the complex ion. If the value of the molar absorptivity constant, ε, can be determined at an appropriate wavelength, many calculations involving this reaction system can be performed, through application of the Beer-Lambert Law:

$$A = \varepsilon \ \ell \ [FeSCN^{2+}] \qquad (2)$$

You should review Appendix I if necessary to again familiarize yourself with this important relation.

The behavior of ions in solution is affected by the overall level of ions present in the solution. This is called the *ionic strength* of the solution. Since studies of equilibrium constants involve quantities like the concentrations of ions (for the complex ion formation reaction above), there is a need to maintain a comparable level of ionic strength in all solutions involved in the experiment. This will be accomplished in this experiment by maintaining the same level of concentration of nitric acid in all of the relevant solutions. As mentioned above, nitric acid causes solutions of Fe^{3+} to be colorless, and it also prevents the unwanted precipitation of $Fe(OH)_3(s)$.

One last complication: a competing reaction. While the nitric acid is useful in eliminating the absorption of visible light by Fe^{3+} ions and in helping maintain comparable levels of ionic strength for this experiment, there is an additional complication that arises. It turns out that thiocyanate ion, SCN^-, reacts with nitric acid, producing various oxidized products. Fortunately, this reaction is quite slow at room temperature, though its effects are certainly noticeable over a period of several minutes. The consequences of this competing reaction on the equilibrium reaction are investigated qualitatively in this experiment.

PROCEDURE:

Part A. Determining the Molar Absorptivity of $FeSCN^{2+}$

1. The absorbance spectrum of a solution containing $FeSCN^{2+}$ ions was provided in the Pre-Lab Exercises. Solutions of the other two species involved in the complex ion formation reaction are in the laboratory. Based on your Pre-Lab work and observation of these solutions, determine an appropriate wavelength for use in this equilibrium study.

2. Obtain 10 mL each of the 0.0200 M Fe^{3+} and 0.000200M KSCN solutions into two clean, dry 50 mL beakers. Into each beaker place a dedicated disposable plastic pipet to be used ONLY for transferring that solution (be careful not to mix them up!)

3. Use pipets to add 1.00 mL of 2.0 M HNO_3 and 1.00 mL of 0.000200 M KSCN solutions into a clean, dry cuvette. Agitate the cuvette to mix well. Use this solution as a blank while calibrating the Spectronic-200 at the selected wavelength, using the supplied instructions.

4. Obtain about 0.3 g of solid $Fe(NO_3)_3 \cdot 9H_2O$. Add a few granules of this material to the solution in the cuvette. Mix the solution by pulling the liquid up into a disposable pipet and then reintroducing the liquid from the pipet to the cuvette. Repeat this until the granules are completely dissolved. Measure and record the absorbance. Continue adding a few granules at a time in this manner, measuring and observing the absorbance until all 0.3 g have been added, or until the readings stop changing. Record the final Absorbance reading on the Data Sheet. Discard this solution in the sink, flushing with water.

✍ **Answer in-lab questions #1 and #2 on page 4.**

Part B. More Examples of LeChatelier's Principle

1. Place the Spectronic 200 in %T mode.

2. Into a clean, dry test tube, measure 2.00 mL of 0.0200 M Fe^{3+} solution (dissolved in 1 M HNO_3) and 2.00 mL of 0.000200 M KSCN. After mixing well, fill a clean, dry cuvette about 2/3 full with this solution. Measure and record the percent transmittance.

✍ **Answer in-lab questions #3 and #4 on page 4.**

3. To a clean, dry test tube, add 2.00 mL of 0.0200 M Fe^{3+} solution (dissolved in 1 M HNO_3) and 2.00 mL of 0.000200 M KSCN. To this mixture, carefully add 1.00 mL 2.0 M HNO_3 and 3.00 mL of distilled water from the burets provided. After mixing well, fill a clean, dry cuvette about 2/3 full with this solution. Measure and record the percent transmittance.

✍ **Answer in-lab question #5 on page 5.**

4. To a clean, dry test tube, add 2.00 mL of 0.0200 M Fe^{3+} solution (dissolved in 1 M HNO_3) and 1.00 mL of 0.000200 M KSCN. To this mixture, carefully add 1.00 mL of distilled water from the burets provided. After mixing well, fill a clean, dry cuvette about 2/3 full with this solution. Measure and record the percent transmittance.

✍ **Answer in-lab questions #6 and #7 on page 5.**

5. With the last solution still in the Spec 200 instrument, drop a few crystals of solid KSCN into the cuvette and note any changes to the percent transmittance.

After you have completed all of the in-lab questions, hand in your lab.

Name____________________________ Section____________________________

Partner____________________________ Date______________________________

DATA SECTION - Part A & B
Experiment 12H

INCLUDE UNITS AND APPROPRIATE SIGNIFICANT FIGURES.

Part A. Determining Molar Absorptivity of $FeSCN^{2+}$

Wavelength Selected: ________________

Absorbance of solution after a few granules of $Fe(NO_3)_3 \cdot 9H_2O$ added: ________________

Absorbance of solution upon completion of $Fe(NO_3)_3 \cdot 9H_2O$ addition: ________________

Part B. More Examples of LeChatelier's Principle

	Step B.2	Step B.3	Step B.4
Measured percent transmittance			
Calculated Absorbance			

Observations following addition of solid KSCN from step B.5:

Name ______________________________ Section ____________

✍ IN-LAB QUESTIONS – Parts A and B ✍
Experiment 12H

Complete these questions during lab.

1. Using guidance from Pre-Lab questions 3a and 3b, calculate the molar concentration of $FeSCN^{2+}$ in the solution that resulted at the end of Part A, step 4. How does LeChatelier's principle justify your calculation?

2. Based on the [$FeSCN^{2+}$] just determined, and the absorbance of the solution measured at the end of Part A, step 4, determine the molar absorptivity, ε, of the $FeSCN^{2+}$ at the selected wavelength. Verify with your instructor that this value has been correctly determined. (Note: your result should be comparable to the value calculated in Pre-Lab question 2, but be sure to use your <u>experimental</u> value for future work.)

3. Use your <u>experimental</u> value of the molar absorptivity, ε, for $FeSCN^{2+}$, and the absorbance calculated for Part B, step 2, to calculate the equilibrium concentration of $FeSCN^{2+}$ in the solution.

4. Set up an ICE table to show the initial, change and equilibrium concentrations of all species in the solution of Part B, step 2. Calculate the value of K. Verify with your instructor that this value has been correctly determined.

5. Set up an ICE table and calculate the value of the equilibrium constant K, using the new initial conditions and experimental absorbance from step 3. Verify with your instructor that this value has been correctly determined.

6. Set up a new ICE table for the mixture of step 4 and again calculate K.

7. Compare the K values from the three experiments. **Should they, in principle, be the same?**

8. a) Use LeChatelier's Principle to predict how the absorbance will change if extra solid KSCN were added to the equilibrium mixture just measured. Is this consistent with your observations?

   b) Finally, as mentioned in the Discussion section, thiocyanate ion SCN^- reacts slowly in nitric acid. This reaction is not part of the complex ion formation reaction, but the gradual disappearance of the SCN^- reactant affects the equilibrium of the complex ion formation reaction. What does LeChatelier's Principle imply about the effect of this slow reaction on the absorbance value for solutions like the one in the cuvette?

OPTIONAL QUESTIONS (Instructor's choice):

1. While adding the solid $Fe(NO_3)_3{\cdot}9H_2O$, the volume of the solution increased slightly, though this was ignored in the calculation. Is your calculated value of the molar absorptivity greater than, less than or the same as the actual molar absorptivity? Explain.

2. For an endothermic reaction where only one of the *reactants* absorbs visible light, explain whether a solution in which this reaction is at equilibrium will fade or intensify as the temperature increases.

3. Determine the concentration of the complex ion $FeSCN^{2+}$ in the solution at the end of Part A, step 3 of the procedure, i.e., after all 0.3 g of the iron nitrate compound have been dissolved in the solution. Use the value of K determined in the other calculations, and assume no volume change in the solution while adding the solid iron nitrate compound. How does this concentration compare with the concentration you assumed for determining the value of the molar absorptivity constant ε?

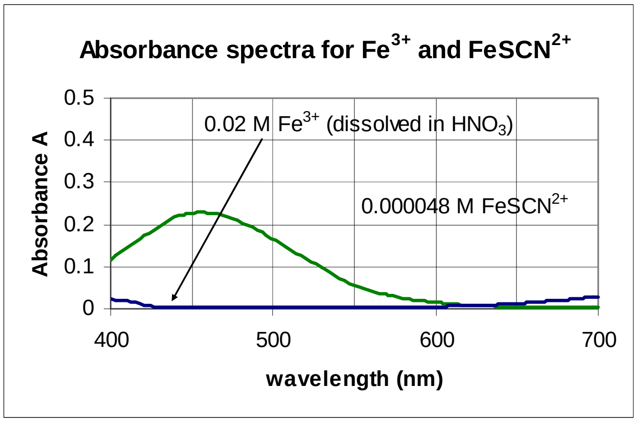
4. The solution of Part B, step 2 has a certain ionic strength which must be maintained in all other solutions involved in this experiment, since we want to be able to treat K as a true constant for a given temperature. The ionic strength is dominated by the nitric acid in these experiments. What is the concentration of the nitric acid in this solution? Calculate the nitric acid concentrations for the solutions in steps 3 & 4 to confirm they have the same concentration as the solution in step 2.

Name ____ Date __________________

PRE-LAB QUESTIONS
Experiment 12H

Complete these questions prior to attending lab. Some of the results will be useful in conducting the experiment, so you should record those results in the appropriate section of the lab as well.

1. In Part A, step 1, you are directed to set up the Spectronic 200 instrument for measurement of the $FeSCN^{2+}$ product ion. Based on the spectra below, what would be an appropriate wavelength for the measurement? Review Appendix I if necessary to again familiarize yourself with the issues related to this decision. Briefly explain your choice.



2. In Part A, step 4, you will experimentally determine the value of the molar absorptivity, ε, for $FeSCN^{2+}$ at your selected wavelength. Using the Beer-Lambert law, calculate an approximate value for ε based on the spectrum of 0.000048 M $FeSCN^{2+}$ provided above. The pathlength, ℓ, for the cuvette is 1.00 cm.

3a. In Part A, step 4, you add about 0.3 g of solid $Fe(NO_3)_3{\cdot}9H_2O$ to a cuvette containing 1.00 mL of 2.0 M HNO_3 and 1.00 mL of 0.000200 M KSCN. Assuming no reaction, what will be the initial molar concentrations of Fe^{3+} and SCN^- in the resulting solution? (Don't forget the dilution effect!)

b. Assuming the reaction $Fe^{3+}(aq) + SCN^-(aq) \rightarrow FeSCN^{2+}(aq)$ goes completely to the right, what will be the molar concentration of $FeSCN^{2+}(aq)$ in the solution resulting from Part A, step 4? (Think about the limiting reactant!)