Experiment 12H

FV 5/16/12

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-20, cuvettes, 10-mL graduated cylinders, 1-mL and 2-mL volumetric pipets, graduated pipet, digital thermometer and rubber-stopper holder, ice, 400-mL beaker, 50-mL beakers, small plastic weighing dish

PURPOSE: The purpose of this experiment is to determine the equilibrium constant K and illustrate LeChatelier's Principle and to determine the standard thermodynamic quantities ΔH^o, ΔG^o, and ΔS^o for a chemical reaction.

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.
4. Calibrate a thermometer, and apply the calibration correction to all temperature readings.
5. Determine the value of the equilibrium constant for a reaction at a variety a temperatures, and from this data, determine the ΔH^o for the reaction.
6. Determine the values of K, ΔG^o, and ΔS^o for a reaction, based on these same measurements.

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

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

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. This provides a significant advantage for the experimenter. If the value of the molar absorptivity constant, ε, can be determined at an appropriate wavelength, a door is opened to performing many calculations involving this reaction system, through application of the Beer-Lambert Law:

$$A = \varepsilon \, \ell \, [FeSCN^{2+}] \tag{2}$$

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

The issue of ionic strength (again!). In a couple of other experiments this semester, the concept of ionic strength has been mentioned without much elaboration. Put simply, the behavior of ions in solution is affected by the overall level of ions present in 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.

The Equilibrium Constant K, LeChatelier's Principle and Thermodynamics. General chemistry texts provide extensive coverage of the main concepts illustrated by this experiment. These include the general features of chemical equilibrium, using reaction tables (usually called "ICE tables") to relate concentrations, stoichiometry and K and discussions of LeChatelier's Principle. On the thermodynamics side this includes the concept of changes in free energy (ΔG) and its relationship to the equilibrium constant. Students are referred to their textbooks for further information on these topics.

Experimental access to the thermodynamic quantities ΔH^o, ΔG^o and ΔS^o is gained by measuring the equilibrium constant for a reaction at several different temperatures. Qualitatively, an increase in temperature for an <u>endo</u>thermic reaction makes the process more product-favored, and so K_c increases. On the other hand, increasing the temperature for an <u>exo</u>thermic reaction leads to a decrease in K_c; the reaction becomes <u>less</u> product-favored at higher temperatures. This behavior can be quantified with the relationship

$$\ln K_T = \frac{-\Delta H^o}{R}\left(\frac{1}{T}\right) + C \tag{3}$$

where ΔH^o has been assumed to be constant with respect to temperature and C is an arbitrary constant, and K_T just represents K_c at the temperature of interest. Thus Eq. (3) provides the direct connection between this type of experimental data and the thermodynamic quantity ΔH^o. A plot of the data points in the form of ln K_T vs. 1/T will generally follow a straight-line trend, and the slope of the best-fit straight line will correspond to the quantity $-\Delta H^o/R$. In earlier chapters, we learned of other methods, involving calorimetry, for obtaining the enthalpy change for reactions. The connection to ΔG^o is then made through the equation

$$\Delta G_T^o = -RT \ln K_T^o \tag{4}$$

Since ΔG^o is <u>not</u> constant with respect to temperature, the temperature must be specified when reporting its value. The temperature of 25°C (298.15 K) is often chosen for this reporting temperature. All that is needed is the value of the equilibrium constant K at 298.15 K, which can easily be obtained from the graph and trend-line discussed above. Finally, the quantity ΔS^o can be obtained from the equation

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{5}$$

since the values of ΔH^o and ΔG^o are known already. With the value for ΔG^o at a given temperature, it is possible to predict the spontaneous reaction direction for any set of conditions through the use of the equation

$$\Delta G = \Delta G^o + RT \ln Q \tag{6}$$

It is one of the remarkable achievements of science to be able to obtain so much information about the behavior of reaction systems via such limited data. This experiment provides an opportunity for students to accomplish this for themselves via simple physical measurements and relationships such as the Beer-Lambert Law. Heat production (or absorption), entropy changes, and predictions about spontaneity are issues that are all resolved through this simple, yet elegant, approach.

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. Set the filter and wavelength on the Spectronic 20 instrument to the appropriate values.

2. Use pipets to add 2.00 mL each of 2.0 M HNO_3 and 0.000200 M KSCN solutions to a clean, dry cuvette. Agitate the tube to mix well. First, use this solution as a blank while calibrating the Spectronic-20 at the selected wavelength.

3. Obtain about 0.6 g of solid $Fe(NO_3)_3 \cdot 9H_2O$. Add a few granules of this material to the solution in the cuvette and mix until the granules are completely dissolved. Measure and record the absorbance. Continue adding a few granules at a time in this manner, measuring and recording the absorbance until all 0.6 g have been added, or until the readings stop changing. Discard this solution in the sink, flushing with water.

✍ **Answer in-lab questions #1 and #2 on page 5.**

Part B. More Examples of LeChatelier's Principle

1. To a clean, dry cuvette, 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. After mixing well, measure and record the absorbance.

✍ **Answer in-lab questions #3 and #4 on page 5.**

2. To the cuvette from step B.1, add 1.00 mL 2.0 M HNO_3 and 3.00 mL of distilled water. Mix well and measure the absorbance to verify (or not) your prediction from the Pre-Lab exercises.

✍ **Answer in-lab question #5 on page 6.**

3. To a clean, dry cuvette, add 2.00 mL of 0.0200 M Fe^{3+} solution (dissolved in 1 M HNO_3), 5.00 mL of 0.000200 M KSCN and 1.00 mL of 2.0 M HNO_3. After mixing well, measure and record the absorbance.

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

4. With the last solution still in the Spec 20 instrument, drop a few crystals of solid KSCN into the cuvette and note any changes to the absorbance. Then, check your prediction about the effect of the loss of SCN^- by reaction with HNO_3 by leaving the solution in the spectrophotometer for a few minutes, observing the reading. How did the observations compare to your predictions?

After you have completed all of the in-lab questions, hand in your lab. You will get it back in time for Part C.

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

Absorbance after mixing 0.0200 M Fe^{3+} with 0.000200 M KSCN: ________________

	Step B.2	Step B.3
Measured absorbance		

Observations following addition of solid KSCN from step B.4:

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 3. 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 3, 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 measured in Part B, step 1, 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 1. Calculate the value of K. Verify with your instructor that this value has been correctly determined.

5. Set up an ICE table and recalculate the value of the equilibrium constant K, using the new initial conditions and experimental absorbance from step 2. Verify with your instructor that this value has been correctly determined.

6. Set up a new ICE table for the mixture of step 3 and again recalculate K. Compare the K values from the three experiments. **Should they, in principle, be the same?**

7. a) Use LeChatelier's Principle to predict how the absorbance will change if extra solid KSCN were added to the equilibrium mixture just measured.

   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. What does this indicate about the calculated value of the molar absorptivity? Explain.

2. Explain how the reaction of the SCN^- with nitric acid, discussed in Part B, step 4, affects the results of this experiment, and whether these effects are significant or not.

3. 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.

4. 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 0.6 g of the iron nitrate compound have been dissolved in the solution. Use the value of K at 298.15 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?

5. The solution of Part B, step 1 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 2 & 3 to confirm they have the same concentration as the solution in step 1.

Part C. Determining ΔH^o, ΔG^o, and ΔS^o for the Complex Ion Formation Reaction

(You have performed the following procedure in Exp. 12H, Parts A and B. You will need to set up the Spec 20 spectrometers in exactly the same way as you did previously. Look over your earlier work to find the proper wavelength, the ε value of the product, the volumes of solutions used, etc.)

1. Set the wavelength and filter of the spectrometer to the same positions as you used in Parts A and B of this experiment.

2. Use pipets to add 2.00 mL each of 2.0 M HNO_3 and 0.000200 M KSCN solutions to a clean, dry cuvette. Agitate the tube to mix well. First, use this solution as a blank while calibrating the Spectronic-20 at the selected wavelength.

3. Adjust the rubber stopper on the thermometer so that the tip of the thermometer is between about ½ and ¾ inch above the bottom of a cuvette when the rubber stopper is seated on the top of the cuvette.

4. Add 2.0 ml of 0.0200 M Fe^{3+} (in 1.0 M HNO_3) solution to the solution made in step 2 and mix well. Place the cuvette in the ice bath until the solution temperature is around 4°C.

5. Dry off the cuvette, making sure that no condensation forms on the side. Read the temperature, take the thermometer out of the cuvette and place the cuvette in the spectrophotometer. Read the absorbance.

6. Take the cuvette out of the spectrophotometer and put the thermometer back in the cuvette. When the temperature has increased by 4°C, record the temperature and remove the thermometer. Wipe off any condensations and place the cuvette into the spectrophotometer and read the absorbance. Repeat this step until 5 readings at 5 different temperatures have been recorded (in temperature increments of about 4°C).

7. Put hot water from the tap into a 50-mL beaker. Put your cuvette into the warm water. Put the thermometer into the cuvette. When the temperature of your mixture in the cuvette is ~35°C, remove the cuvette, wipe the water off the sides of the cuvette and measure the absorbance. Record the temperature of the mixture.

Clean-Up:

1. Discard all solutions down the drain with running water.

2. Clean all glassware and pick up all paper litter.

DATA SECTION – Part C

Part C. Determining ΔH^o, ΔG^o, and ΔS^o for the Complex Ion Formation Reaction

Wavelength Selected: _______________

%T Measurements at Various Temperatures	Temperature °C	Absorbance
Measuring point #1		
Measuring point #2		
Measuring point #3		
Measuring point #4		
Measuring point #5		
Measuring point #6		

DATA ANALYSIS (Part C):

1. Use your data from Part C and determine the value of the equilibrium constant K at each different temperature measured. Be sure to use corrected temperatures in each case.

2. Create a plot of ln K vs 1/T and use it to determine ΔH^o for the reaction (assumed to be independent of temperature).

3. Use the trendline from your plot to find the value of K at 298.15K. Use this to determine ΔG^o at 298.15K for the reaction.

4. Combine your results to obtain ΔS^o for the reaction.

5. Attach an Excel spreadsheet to your lab that contains your plot and all calculated values. Organize and clearly label your spreadsheet (remember significant figures and units!!). Do **not** use a spreadsheet from another mid (including your partner) as a template for this lab.

QUESTIONS:

1. Using your experimental values for ΔH^o, ΔG^o, and ΔS^o for the complex ion formation reaction, determine the ΔH_f^o, ΔG_f^o and S^o for the $FeSCN^{2+}$ species at 25°C, given the corresponding values for the thiocyanate ion, SCN^- and Fe^{3+} ion in the table below.

	ΔH_f^o (kJ/mol)	**ΔG_f^o (kJ/mol)**	**S^o (J/mol K)**
SCN^-	76.4	92.7	144.3
Fe^{3+}	-47.7	-10.5	293.3

$\Delta H_f^o(FeSCN^{2+})$ ____________ $\Delta G_f^o(FeSCN^{2+})$ ____________ $S^o(FeSCN^{2+})$ ____________

2. Suppose a solution could be made with the following ionic species concentrations at 25°C: $[Fe^{3+}] = 0.0015$ M, $[SCN^-] = 0.0010$ M, and $[FeSCN^{2+}] = 0.00080$ M. Using the results of your experiment, determine whether this system is at equilibrium or, if not, in which direction the reaction would spontaneously proceed. Would the intensity of the color of the solution increase or decrease as equilibrium was approached?

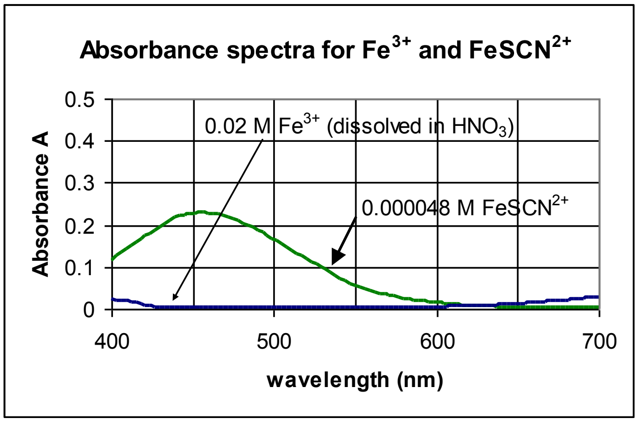
3. A water sample is to be tested for the presence of Fe^{3+} ions. To 10.0 mL of water is added some nitric acid and a high concentration of SCN^-, resulting in a new total volume of 15.0 mL. The solution becomes slightly red in color. The %T at the wavelength used in this experiment was found to be 85.6%. From this information, and using your experimentally determined molar absorptivity ε, determine the molarity and ppm of Fe^{3+} in the sample.

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 20 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 3, 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 3, you add about 0.6 g of solid $Fe(NO_3)_3{\cdot}9H_2O$ to a cuvette containing 2.00 mL of 2.0 M HNO_3 and 2.00 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 3? (Think about the limiting reactant!)

4a. In Part B, step 2, you will double the volume of an equilibrium solution, and examine the effect. You should be able to predict what will happen when the equilibrium concentrations of all species in the reaction

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

are cut in half as the volume is doubled. According to LeChatelier's Principle, in which direction will the reaction shift as a result of the dilution?

b. Will the absorbance of the solution increase or decrease as a result of the dilution? Will the final absorbance reading of the solution be higher or lower than one-half the value that existed before the dilution? Briefly explain your answer.