Experiment 12H

PRINCIPLES OF EQUILIBRIUM AND THERMODYNAMICS

MATERIALS: 0.0200 M Fe(NO₃)₃ in 1 M HNO₃, 0.000200 M KSCN, 2.0 M HNO₃, solid Fe(NO₃)₃·9H₂O with accompanying spatula, solid KSCN, Spectronic-200, cuvettes, 10-mL graduated cylinders, 1-mL and 2-mL volumetric pipets, graduated pipet, digital thermometer, 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°, ΔG°, and ΔS° 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. Determine the value of the equilibrium constant for a reaction at a variety of temperatures, and from this data, determine the ΔH° for the reaction.
5. Determine the values of K, ΔG°, and ΔS° 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

Fe³⁺(aq) + SCN⁻(aq) ⇄ FeSCN²⁺(aq) (1)

Associated with this reaction is an equilibrium constant K, which varies with temperature depending on the exo- or endothermicity of the reaction. The product of this reaction is a complex ion, FeSCN²⁺, 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 Fe³⁺ 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 = ε ℓ [FeSCN²⁺] (2)

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

The issue of ionic strength (again!). In 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 Fe³⁺ 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 Fe³⁺ 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 ∆H°, ∆G° and ∆S° is gained by measuring the equilibrium constant for a reaction at several different temperatures. Qualitatively, an increase in temperature for an endothermic reaction makes the process more product-favored, and so K increases. On the other hand, increasing the temperature for an exothermic reaction leads to a decrease in Kc; the reaction becomes less product-favored at higher temperatures. This behavior can be quantified with the relationship

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

(3)

where ∆H° has been assumed to be constant with respect to temperature and C is an arbitrary constant, and K_T just represents K at the temperature of interest. Thus Eq. (3) provides the direct connection between this type of experimental data and the thermodynamic quantity ∆H°. 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 -ΔH°/R. In earlier chapters, we learned of other methods, involving calorimetry, for obtaining the enthalpy change for reactions. The connection to ∆G° is then made through the equation

\[
\Delta G^o_T = -RT \ln K^o_T
\]

(4)

Since ∆G° is not 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 ∆S° can be obtained from the equation

\[
\Delta S^o = \Delta H^o - T \Delta S^o
\]

(5)

since the values of ∆H° and ∆G° are known already. With the value for ∆G° at a given temperature, it is possible to predict the spontaneous reaction direction for any set of conditions through the use of the equation

\[
\Delta G = \Delta G^o + RT \ln Q
\]

(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.

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. Assuming solution densities of 1.00 g/mL, use a top-loading balance to weigh out 1.00 mL (1.00 ± 0.02 g) each of 2.0 M HNO\(_3\) and 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\(_3\))\(_3\)-9H\(_2\)O. 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 5.

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 using the top-loading balance as described above. 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 5.

3. To a clean, dry test tube, add 1.00 mL of 0.0200 M Fe\(^{3+}\) solution (dissolved in 1 M HNO\(_3\)), 1.00 mL of 0.000200 M KSCN using the top-loading balance as described above. To this mixture, carefully add 0.50 mL 2.0 M HNO\(_3\) and 1.50 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 6.

4. To a clean, dry test tube, add 2.00 mL of 0.0200 M Fe\(^{3+}\) solution (dissolved in 1 M HNO\(_3\)), 1.00 mL of 0.000200 M KSCN using the top-loading balance as described above. To this mixture, carefully add 1.00 mL 2.0 M HNO\(_3\) 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 6.

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. You will get it back in time for Part C.
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$_3$)$_3$·9H$_2$O added: __________

Absorbance of solution upon completion of Fe(NO$_3$)$_3$·9H$_2$O addition: __________

**Part B. More Examples of LeChatelier’s Principle**

<table>
<thead>
<tr>
<th></th>
<th>Step B.2</th>
<th>Step B.3</th>
<th>Step B.4</th>
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<tbody>
<tr>
<td>Measured percent transmittance</td>
<td></td>
<td></td>
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<tr>
<td>Calculated Absorbance</td>
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</tbody>
</table>

Observations following addition of solid KSCN from step B.5:
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 4, determine the molar absorptivity, $\varepsilon$, 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 experimental value for future work.)

3. Use your experimental value of the molar absorptivity, $\varepsilon$, 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.

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(NO₃)₃·9H₂O, 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. Explain how the reaction of the SCN⁻ with nitric acid, discussed in Part B, step 5, 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 FeSCN²⁺ 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 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 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.
Part C. Determining $\Delta H^o$, $\Delta G^o$, and $\Delta S^o$ 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 200 spectrometers in exactly the same way as you did previously. Look over your earlier work to find the proper wavelength, the $\varepsilon$ 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. Use this solution as a blank for calibrating the Spectronic-200 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. To another clean, dry cuvette add 2.0 mL of 0.0200 M Fe$^{3+}$ (in 1.0 M HNO$_3$) solution to 2.0 mL of 0.000200 M KSCN 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 $\Delta H^o$, $\Delta G^o$, and $\Delta S^o$ for the Complex Ion Formation Reaction

Wavelength Selected: _____________

<table>
<thead>
<tr>
<th>%T Measurements at Various Temperatures</th>
<th>Temperature °C</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measuring point #1</td>
<td></td>
<td></td>
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<tr>
<td>Measuring point #2</td>
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<td>Measuring point #5</td>
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<tr>
<td>Measuring point #6</td>
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</table>
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 $\Delta H^o$ 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 $\Delta G^o$ at 298.15K for the reaction.

4. Combine your results to obtain $\Delta S^o$ 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 $\Delta H^o$, $\Delta G^o$, and $\Delta S^o$ for the complex ion formation reaction, determine the $\Delta H^o$, $\Delta G^o$, and $\Delta S^o$ 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.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^o$ (kJ/mol)</th>
<th>$\Delta G^o$ (kJ/mol)</th>
<th>$S^o$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCN$^-$</td>
<td>76.4</td>
<td>92.7</td>
<td>144.3</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>-47.7</td>
<td>-10.5</td>
<td>293.3</td>
</tr>
</tbody>
</table>

$\Delta H^o$(FeSCN$^{2+}$)  $\Delta G^o$(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 $\varepsilon$, determine the molarity and ppm of Fe$^{3+}$ in the sample.
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.

![Absorbance spectra for Fe\(^{3+}\) and FeSCN\(^{2+}\)](image)

2. In Part A, step 4, you will experimentally determine the value of the molar absorptivity, \(\varepsilon\), for FeSCN\(^{2+}\) at your selected wavelength. Using the Beer-Lambert law, calculate an approximate value for \(\varepsilon\) based on the spectrum of 0.000048 M FeSCN\(^{2+}\) provided above. The pathlength, \(\ell\), 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\(_2\)O 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!)