Experiment 12I

PRINCIPLES OF EQUILIBRIUM

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, spectrophotometer, cuvettes, burets, 50-mL beakers (2), small plastic weighing dish

PURPOSE: The purpose of this experiment is to determine the equilibrium constant K and illustrate LeChatelier's Principle 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 using ICE tables 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.

INTRODUCTION:

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:

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

Associated with this reaction is an equilibrium constant K, the value of which expresses the relative amounts of reactants and products present in the equilibrium mixture. 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.

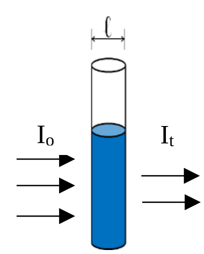

Figure 1. transmittance of light through a solution in a cuvette.

Beer-Lambert Law. Because reaction (1) involves a colored substance, the reaction can be studied using spectrophotometry, an analytical technique used to measure the amount of light absorbed by a substance (or substances) in solution. This is illustrated in Figure 1. I_o and I_t are the incident and transmitted intensity of light, respectively, through a solution of path length ℓ. The amount of light transmitted through a solution can be expressed as the percent transmittance, %T, which is simply (I_t/I_o) x 100. Note that %T has no units because the units of intensity cancel. Absorbance, A, is defined as follows:

$$A = -\log\left(\frac{\%T}{100}\right) \qquad (2)$$

Depending on the spectrophotometer used, you will measure %T and/or A. The latter is needed to determine the molar concentration of the absorbing species, c, through the Beer-Lambert law:

$$A = \varepsilon \cdot \ell \cdot c \quad (3)$$

where ε is the molar absorptivity. Note that it is the absorbance that is directly proportional to the concentration, not the percent transmittance. The molar absorptivity, ε, is unique for an absorbing species at a particular wavelength. In other words, if a substance does not absorb light at a certain wavelength, ε (for that substance) will be zero at that wavelength. If the substance is strongly absorbing at that wavelength, ε will be large. The units of ε are determined from only ℓ and c because absorbance has no units (because of %T). Additional information on the Beer-Lambert law and spectrophotometry is given in Appendix I on the Plebe Chemistry Website:
https://www.usna.edu/ChemDept/_files/documents/manual/ApdxI.pdf.

The issue of ionic strength. The concept of **ionic strength** is related to the **total ion concentration** in solution. Simply put, 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. The "background" ions from the nitric acid is also much higher than the concentrations of the reactant and product ions in the equilibrium being studied. 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 and LeChatelier's Principle. 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. You will use these principles and concepts to experimentally determine the equilibrium constant of reaction (1) starting with different concentrations of reactants at a constant temperature.

PROCEDURE:

Part A. Determining the Molar Absorptivity (ε) 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. Using the buret at the sink station, add 2.00 mL of 0.000200 M KSCN solution into a clean, dry test tube.
3. Add 2.00 mL of 2.0 M HNO_3 (from the supplied buret) to the test tube containing the KSCN solution and agitate it to mix well. Use this solution as a blank while calibrating the spectrophotometer at the selected wavelength, using the supplied instructions.
4. 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 test tube. Mix the solution by pulling the liquid up into a disposable pipet and then reintroducing the liquid from the pipet to the test tube. 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 0.6 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.

Part B. More Examples of LeChatelier's Principle

1. Make sure the spectrophotometer is in absorbance mode. Do not adjust other controls after the instrument is calibrated.
2. Using burets at the sink stations, add 2.00 mL of 0.0200 M Fe^{3+} solution and 2.00 mL of 0.000200 M KSCN to a clean, dry test tube. After mixing well, measure and record the absorbance.
3. Using burets at the sink stations, add 1.00 mL of 0.0200 M Fe^{3+} solution, 2.50 mL of 0.000200 M KSCN, 0.50 mL HNO_3, to a clean, dry test tube. After mixing well, measure and record the absorbance.
4. Using burets at the sink stations, add 1.00 mL of 0.0200 M Fe^{3+} solution,1.00 mL of 0.000200 M KSCN, 0.50 mL of 2.0 M HNO_3 and 1.50 mL of distilled water to a clean dry test tube. After mixing well, measure and record the absorbance. (Do not discard this solution yet!)
5. With the last solution still in the spectrophotometer, drop a few crystals of solid KSCN into the test tube and note any changes to the absorbance.

Clean-Up:

Note: You may want to delay cleaning up until you have calculated the equilibrium constants. If your data is not good, you will have to repeat the experiment.

1. Discard all solutions down the drain with running water.
2. Clean all glassware and pick up all paper litter.
3. Place the cleaned test tubes in the test tube rack, standing upside down.

Name_______________________ Section_______________________

Partner_______________________ Date_________________________

DATA SECTION
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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 absorbance			

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

Name______________________ Section______________________

Partner______________________ Date________________________

DATA TREATMENT
Experiment 12I

1. Using guidance from Pre-Lab questions 3a and 3b on p. E12I-8, 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 $FeSCN^{2+}$ ion 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 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 Part B, step 3.

6. Set up a new ICE table for the mixture of Part B, 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. Explain.

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

b) Finally, as mentioned in the Introduction, 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? Explain.

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

QUESTIONS:

1. Suppose a solution could be made with the following ionic species concentrations at 25°C: $[Fe^{3+}] = 0.0020$ M, $[SCN^{-}] = 0.0015$ M, and $[FeSCN^{2+}] = 0.0015$ 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? Explain.

2. 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 20.0 mL. The solution becomes slightly red in color. The solution was placed in a 1.0 cm pathlength cell, and the %T at the wavelength used in this experiment was found to be 75.6%. Using this information, together with your experimentally determined molar absorptivity (ε) value, calculate the molarity and ppm of Fe^{3+} in the sample.

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Name ____ Date ________________

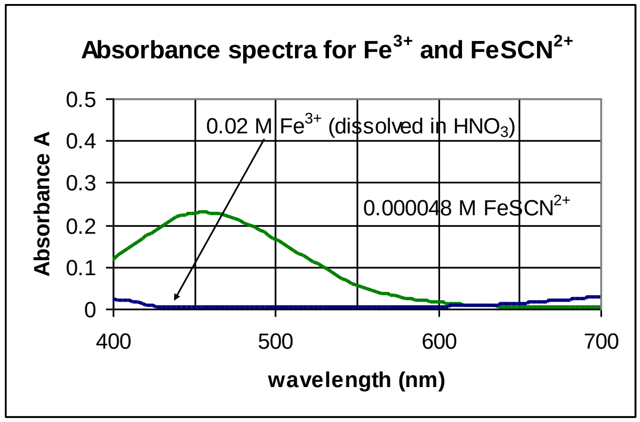
PRE-LAB QUESTIONS
Experiment 12I

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 spectrophotometer for measurement of the $FeSCN^{2+}$ product ion.

   a. Based on the spectra given here, 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.

   b. Briefly explain your choice.



2. In Part A, step 5, 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.

3. In Part A, step 4, 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.

   a. Assuming no reaction, what will be the initial molar concentrations of Fe^{3+} and SCN^- in the resulting mixture? (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!)