Experiment 12I

FV 8/21/2020

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, 10-mL graduated cylinders, buret, digital thermometer, 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 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.

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

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

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.

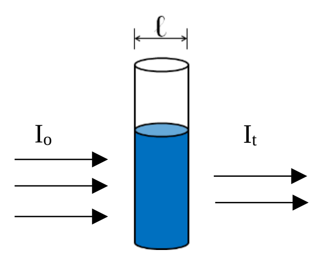


Figure 1. transmittance of light through a solution in a cuvette.

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 $(I_t/I_o) \times 100$. Note that %T has no units because the units of intensity cancel. Absorbance, A, is defined as

$$A = -\log\frac{\%T}{100} \quad (2)$$

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:

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

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.

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. 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. Obtain 10 mL each of the 0.0200 M Fe^{3+} and 0.000200 M 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 2.00 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 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 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 0.6 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.

2. Fill the buret with ≈10 mL of distilled water.

3. Into a clean, dry test tube, weigh out 2.00 mL of 0.0200 M Fe^{3+} solution 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 absorbance.

4. To a clean, dry test tube, add 1.00 mL of 0.0200 M Fe^{3+} solution and 1.00 mL of 0.000200 M KSCN using the top-loading balance as described above. To this mixture, carefully add 0.50 mL of 2.0 M HNO_3 and 1.50 mL of distilled water from the burets. After mixing well, fill a clean, dry cuvette about 2/3 full with this solution. Measure and record the absorbance.

5. To a clean, dry test tube, add 1.00 mL of 0.0200 M Fe^{3+} solution and 2.50 mL of 0.000200 M KSCN using the top-loading balance as described above. To this mixture, add 0.50 mL HNO_3. After mixing well, fill a clean, dry cuvette about 2/3 full with this solution. Measure and record the absorbance.

6. With the last solution still in the spectrophotometer, drop a few crystals of solid KSCN into the cuvette 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
Experiment 12I

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.3	Step B.4	Step B.5
Measured absorbance			

Observations following addition of solid KSCN from step B.6:

Name____________________________ Section____________________________

Partner____________________________ Date______________________________

DATA TREATMENT
Experiment 12I

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 for Part B, step 3, 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 3. 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 4.

6. Set up a new ICE table for the mixture of Part B, step 5 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.

   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.

QUESTIONS:

1. 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?

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 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.

OPTIONAL QUESTIONS

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. Explain how the reaction of the SCN^- with nitric acid, discussed in Part B, step 6, 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 4 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 3 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 Part B, steps 4 & 5 to confirm they have the same concentration as the solution in step 3.

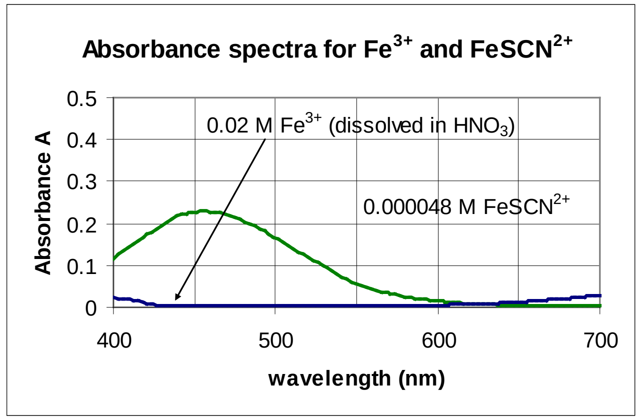
Name ____ Date ___________________

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 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.

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 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!)