Evaluating the Equilibrium Constant for the Reaction of Iron(III) Ion with Thiocyanate Ion

Adapted from Conrad H. Bergo, Michael P. Doherty, William M. Loffredo, and Robert F. Schramm, East Stroudsburg University

Experiment Overview

Use spectrophotometric techniques to evaluate the equilibrium constant for the reaction of iron(III) ion with thiocyanate ion. Determine the equilibrium constants for five equilibrium mixtures prepared using solutions of these two ions with varying concentrations. Compare the five constants to determine a mean equilibrium constant for this reaction.

Background Information

Chemists often need to be able to predict the mass of products that could form from the reactants in a particular chemical reaction. To do so, we often employ a limiting reagent calculation. These calculations are based on the following assumptions: that the chemical reaction goes to completion, and that the reaction proceeds until the limiting reagent is completely converted into products. These calculations often produce inaccurate results. This is because, rather than proceeding to completion, many reactions are reversible. In reversible reactions, while reactants are forming products, some of the products are reverting into reactants. We symbolize reversibility in chemical equations using double arrows (⇌). In reversible reactions, the rate of the forward reaction depends on the concentrations of reactants; the rate of the reverse reaction depends on the concentrations of the products. At first, the high reactant concentrations cause a rapid forward reaction. As the forward reaction proceeds, however, reactant concentrations decrease as reactants change into products. Therefore, the forward reaction rate gradually decreases. At the same time, the increasing product concentrations cause the reverse reaction rate to increase. Eventually, the rates of the forward and reverse reactions become equal. Reactants become products just as rapidly as products change back into reactants. There is no further change in the concentrations of either reactants or products. At this point, we say that the reaction has achieved a state of dynamic equilibrium or simply that the reaction is at equilibrium.

Formation of the Isothiocyanatoiron(III) Ion

In acidic solution, iron(III) ion (Fe^{3+} or ferric ion) reversibly bonds to thiocyanate ion (SCN^-), forming a purple-red coordination ion, as shown in the balanced equation below. Some scientists write the product formula as $FeSCN^{2+}$. However, there is evidence that the covalent bond actually forms between the iron and the nitrogen atoms, making the formula $FeNCS^{2+}$ more accurate. $FeNCS^{2+}$ ion is called isothiocyanatoiron(III) ion. In this experiment, we will measure the equilibrium constant (K_{eq}) for this reaction.

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

For this experiment, we use a solution of iron(III) nitrate, as a source of Fe^{3+} ions. A solution of sodium thiocyanate, NaSCN, serves as the SCN^- ion source. Studies show that the Keq for a reaction is somewhat dependent on the total ionic concentration of the equilibrium mixture. Therefore, we prepare all solutions using 0.10 *M* nitric acid (HNO_3) solution as a solvent, rather than water, to ensure that all mixtures have comparable ionic strength.

Spectrophotometrically Measuring the $FeNCS^{2+}$ Ion Concentration

Because dissolved $FeNCS^{2+}$ ions form an intensely colored solution, we can conveniently measure their concentration with an instrument known as a spectrophotometer. First, we will determine the wavelength of maximum absorbance, λ_{max}. To accomplish this, we will vary the wavelength and measure the absorbance for a single (relatively concentrated) sample solution of the compound at each wavelength. Then we will plot the Absorbance vs. the wavelength and find the wavelength where the absorbance is at maximum. We will use this wavelength for all of our subsequent measurements, as it will give us the best resolution. Using this instrument, we can cause light of a selected wavelength to pass through a sample of the equilibrium mixture. The colored solution absorbs some of the light. This absorption decreases the intensity of light reaching a detector, leading to a measurement of absorbance, A. The equation relating absorbance and molar concentration (C), known as **Beer's Law**, is: $\mathbf{A = \varepsilon\, b\, C}$. In this equation, ε is the molar absorptivity coefficient, which indicates how efficiently the absorbing species absorbs light of the chosen wavelength; **b** is the path length, in centimeters, of the light passing through the solution. When the wavelength of the light and the path length through the solution are kept constant, the measured absorbance is directly proportional to the molar concentration of the absorbing species, in this case $FeNCS^{2+}$, in solution.

Beer's Law can be simplified to the form $\mathbf{A = k\,C}$ or $\mathbf{A = k\,[FeNCS^{2+}]}$ for our experiment.

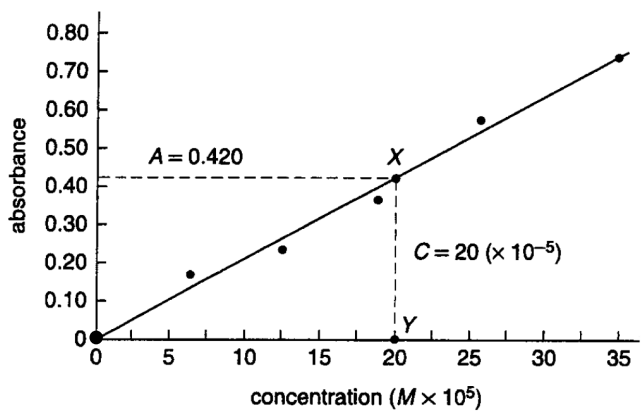

Figure 1 *A Beer's Law plot*

The value k is equal to the slope of the line relating absorbance (no units) and concentration (in *M*). The k value for Beer's Law is not the rate constant, nor is it the equilibrium constant. Because the spectrophotometer is zeroed using a blank (solution containing none of the measured compound), the y-intercept for the graph is zero, and the origin is a measured point to include on the plot.

We can determine the $[FeNCS^{2+}]$ ion concentrations in the equilibrium mixtures using their absorbance data and a calibration plot known as a **Beer's Law plot**. Because absorbance is directly proportional to the molar concentration of the absorbing species, we can expect such a plot to be linear and pass through the origin (0,0). A typical Beer's Law plot is shown in Figure 1.

Preparing a Beer's Law Plot for $FeNCS^{2+}$ Ion

To prepare a Beer's Law plot, we begin by measuring the absorbance of various known $FeNCS^{2+}$ ion concentrations and plot the absorbance at the wavelength of maximum absorbance against the molar concentration of $FeNCS^{2+}$ ion for each solution. (The wavelength of maximum absorbance will be determined in the process of carrying out the experiment.) This experimental approach involves an interesting problem. The reaction which we use to prepare $FeNCS^{2+}$ ion solutions is reversible, so it does not proceed to completion. How, then, can we prepare solutions with known $FeNCS^{2+}$ ion concentrations? To prepare a solution of known $FeNCS^{2+}$ ion concentration, we exploit the equilibrium constant expression for the reaction. If we create an equilibrium mixture in which the Fe^{3+} ion concentration is relatively high, the equilibrium constant expression indicates that the SCN^- concentration for this mixture will be relatively low. Thus, by preparing a solution in which the initial Fe^{3+} ion concentration is much higher than that of SCN^- ion, we can force the reaction to proceed nearly to completion. (Relate this idea to LeChatelier's Principle.) At equilibrium, the SCN^- ion concentration will drop almost to zero. This situation is similar to a limiting reagent problem, in that the equilibrium $FeNCS^{2+}$ ion concentration approximates the initial SCN^- ion concentration. We may use this approximation to calculate the $FeNCS^{2+}$ ion concentration of each of the **standard solutions** that we will use to prepare our Beer's Law plot in this experiment.

Determining K_{eq} for the Formation of the $FeNCS^{2+}$ Ion

To determine K_{eq} for formation of $FeNCS^{2+}$ ion, we will prepare five **equilibrium reaction mixtures** in which we vary the SCN^- ion concentration while keeping the Fe^{3+} ion concentration constant. These mixtures will have Fe^{3+} and SCN^- ion concentrations of similar magnitude, unlike the standard mixtures we use to prepare the Beer's Law plot. $[Fe^{3+}]_0$ and $[SCN^-]_0$ can be calculated for each reaction mixture based on the stock solution concentration, the volume used, and the total volume of the reaction mixture. We will measure the absorbance of each equilibrium mixture at 447 nm. From the absorbance value, we will calculate the equilibrium $FeNCS^{2+}$ ion concentration for each mixture using the equation for the Beer's Law plot. Finally, we can set up an Initial-Change-Equilibrium (I-C-E) table to calculate the equilibrium Fe^{3+} and SCN^- ion concentrations for each mixture. From the three equilibrium concentrations, the equilibrium constant can be calculated.

Procedure

Chemical Alerts

Caution: All of the solutions in this experiment are mixed with nitric acid and are, therefore, toxic, irritating, and oxidants. Contact with skin can cause burns and skin discoloration. Avoid inhaling the vapors and ingesting these solutions. If your skin contacts the solution, immediately wash affected areas of your skin and clothing. If you spill any solution, immediately notify your laboratory instructor. *As always, wear departmentally approved eye protection while doing this experiment.* If any of the solutions do contact your eyes, get to the eye wash station and begin washing your eyes immediately.

Preparing the Standard Solutions for the Beer's Law Plot

1. Label six 50.00-ml volumetric flasks **S1** through **S6**.
2. Deliver 10.00 mL of 2.00×10^{-1} *M* $Fe(NO_3)_3$ solution into each of the volumetric flasks, as indicated in Table 1.
3. Pipet 1.00, 2.00, 3.00, 4.00, and 5.00 mL of 2.00×10^{-3} *M* NaSCN solution into flasks S2 through S6, respectively (none in flask S1).
4. Add 0.10 *M* nitric acid solution to each volumetric flask until the bottom of the meniscus is even with the etched mark on the flask neck. Stopper the flasks. While holding the stopper firmly in place, invert each flask several times to thoroughly mix the solution.

Table 1. Standard Solutions for $FeNCS^{2+}$ ion Beer's Law Plot

Solution	2.00×10^{-1} *M* $Fe(NO_3)_3$ in 0.10 *M* HNO_3 (mL)	2.00×10^{-3} *M* NaSCN in 0.10 *M* HNO_3 (mL)	total volume of solution (mL) (including additional HNO_3)
S1 (blank)	10.00	0.00	50.00
S2	10.00	1.00	50.00
S3	10.00	2.00	50.00
S4	10.00	3.00	50.00
S5	10.00	4.00	50.00
S6	10.00	5.00	50.00

Determination of the Wavelength of Maximum Absorbance (λ_{max}) for the $FeNCS^{2+}$ Ion:

5. Obtain two cuvettes. Rinse one cuvette with solution S1, discarding the rinse into a waste beaker. Fill the rinsed cuvette with solution S1. This solution will serve as a blank, or reference solution.
6. Wipe the cuvette with a lint-free Kimwipe. Do NOT use paper towels or other wipes or cloths as they can scratch the cuvettes. Insert the cuvette into the sample slot for the blank, labeled B. Be sure to properly align the cuvette in the sample holder. The smooth (clear) sides of the cuvettes will be on the same sides as the holes in the slots – This is where the light passes through! *If you are not sure, ask your instructor.*
7. Rinse the other cuvette with the most concentrated solution (S6). Fill each cuvette with the solution S6, wipe with a Kimwipe, and properly load into sample slot 1. Close the sample holder cover.
8. Set the wavelength to the desired wavelength (start at 360 nm, then increase to 560 nm in 20 nm increments as steps 8-10 are repeated).
   - Press the "set nm" button
   - Enter the desired wavelength, and press "enter".
9. Zero the Spectrophotometer.
   - Press "B" (moves the blank into the measuring position).
   - Press "measure blank" (will set the absorbance reading to zero.)
10. Measure the absorbance of the sample.
    - Press the "1" – *the sample wheel "1", not the keypad "1".*
      (This moves the sample in slot "1" into the measuring position.)
    - Read and record the absorbance.
11. Repeat steps 8-10 for each wavelength to be measured. *Be sure to zero (step 9) for each wavelength*!
12. Prepare a graph of Wavelength *(nm)* on the x-axis vs. Absorbance (no units) on the y-axis and determine λ_{max} before proceeding. Report the value with units in your notebook.

Spectrophotometrically Analyzing the Standard Solutions

13. Obtain six cuvettes. Rinse one cuvette with solution S1, discarding the rinse into a waste beaker. Fill the rinsed cuvette with solution S1. This solution will serve as a blank, or reference solution.
14. Wipe the cuvette with a lint-free Kimwipe. Do NOT use paper towels or other wipes or cloths as they can scratch the cuvettes. Insert the cuvette into the sample holder for the blank, labeled B. Be sure to properly align the cuvette in the sample holder. The smooth (clear) sides of the cuvettes will be on the same sides as the holes in the slots – This is where the light passes through! *If you are not sure, ask your instructor.*
15. Rinse the remaining cuvettes with solutions S2-S6, respectively. Fill each cuvette with the corresponding solution S2-S6, wipe with a Kimwipe, and properly insert into the sample holders 1-5. Close the sample holder cover.
16. Set the wavelength of the spectrophotometer to the λ_{max} previously determined. Select the blank. Press "Measure Blank" to set the blank to zero.
17. Cycle through the remaining solutions S2-S6, recording the absorbance for each.
18. Remove the cuvettes from the sample chamber and pour the solutions inside into the waste beaker. Then thoroughly rinse the cuvettes at least three times with tap water and once with distilled or deionized water. Allow the cuvettes to drain.

Preparing and Analyzing the Equilibrium Mixtures

19. Obtain six clean, dry medium test tubes, and label them E1-E6.
20. Pipet 5.00 mL of 2.00 x 10^{-3} *M* $Fe(NO_3)_3$ solution into each of the test tubes.
21. Pipet the volumes of 2.00 x 10^{-3} *M* NaSCN listed in Table 2 into each of the test tubes.
22. Calculate the amount of 0.10 *M* HNO_3 solution that you must add to each test tube so that the total solution volume is 10.00 mL. Pipet the required amounts of HNO_3 into each test tube. Thoroughly mix the solutions in the test tubes by tightly covering the test tubes with parafilm or a stopper and inverting them several times.

Table 2. Equilibrium Mixtures for $FeNCS^{2+}$ Formation

Solution	2.00 x 10^{-3} *M* $Fe(NO_3)_3$ in 0.10 *M* HNO_3 (mL)	2.00 x 10^{-3} *M* NaSCN in 0.10 *M* HNO_3 (mL)	total volume of solution (mL) (including additional HNO_3)
E1 (blank)	5.00	0.00	10.00
E2	5.00	1.00	10.00
E3	5.00	2.00	10.00
E4	5.00	3.00	10.00
E5	5.00	4.00	10.00
E6	5.00	5.00	10.00

23. Obtain six cuvettes. Rinse one cuvette with solution E1, discarding the rinse into a waste beaker. Fill the rinsed cuvette with solution E1. This solution will serve as a blank, or reference solution.
24. Wipe the cuvette with a lint-free Kimwipe. Do NOT use paper towels or other wipes or cloths as they can scratch the cuvettes. Insert the cuvette into the sample holder for the blank. Be sure to properly align the cuvette in the sample holder.
25. Rinse the remaining cuvettes, with solutions E2-E6, respectively. Fill each cuvette with the corresponding solution E2-E6, wipe with a Kimwipe, and properly insert into the sample holders 1-5. Close the sample holder cover.
26. Set the wavelength of the spectrophotometer to the λ_{max} previously determined. Select the blank. Press "Measure Blank" to set the blank to zero.
27. Cycle through the remaining solutions E2-E6, recording the absorbance for each.
28. Remove the cuvettes from the sample chamber and pour the solutions inside into the waste beaker. Then thoroughly rinse the cuvettes at least three times with tap water and once with distilled or deionized water. Allow the cuvettes to drain.
29. Allow solutions to reach the same temperature (within 1.0 C°). Obtain a thermometer. Measure the temperature of each equilibrium mixture, rinsing and drying the thermometer after each temperature measurement.
30. After your laboratory instructor has checked your data and initialed your notebook, properly discard all solutions in the hazardous waste containers.

Data Analysis & Calculations

Perform the following analyses and calculations, showing work and properly labeling your calculations, graphs, and tables. Record the results into appropriate data/results table(s) that you prepare. Do not simply list results.

Wavelength of Maximum Absorbance (λ_{max}) Determination:

1. As specified in the procedure, prepare a graph of **Wavelength *(nm)*** on the x-axis vs. **Absorbance** (no units) on the y-axis and determine λ_{max}. Report the value with units in your notebook.

Analysis of the Standard Solutions

2. Calculate the initial molar SCN^- ion concentrations for the six standard solutions. Assume that NaSCN is completely dissociated, that is, $[SCN^-]_0$ = [NaSCN].
3. Calculate the equilibrium molar $FeNCS^{2+}$ ion concentrations for the standard solutions. Assume all SCN^- ions are complexed with Fe^{3+} ion to form $FeNCS^{2+}$ ion and that $[FeNCS^{2+}]_{final} = [SCN^-]_0$.
4. Prepare a Beer's Law plot for the standard solutions, using the MS Excel or other graphing software. Include the trendline, trendline equation, and R^2 value on the chart. If it appears reasonable based on the data, check the box to require the trendline to pass through the origin.
5. Report the equation in the form of the Beer's Law equation for this specific experiment. Be sure to include units on k.

Analysis of the Equilibrium Mixtures

6. Calculate $[Fe^{3+}]_0$ and $[SCN^-]_0$ for solutions E2-E6.
7. For each equilibrium solution, determine the $[FeNCS^{2+}]_{eq}$ from the Beer's Law Equation.
8. Calculate the $[Fe^{3+}]_{eq}$ and $[SCN^-]_{eq}$ for each solution, E2-E6.
   - As a method of showing the calculations for $[Fe^{3+}]_{eq}$ and $[SCN^-]_{eq}$, prepare a stoichiometry table (Initial-Change-Equilibrium, I-C-E) for ***one*** of the five equilibrium mixtures.
9. Write the equilibrium constant equation for the reaction studied, and calculate K_{eq} for solutions E2-E6. *There is no K value to calculate for E1, as it is the blank.*
10. Calculate the mean K_{eq} and the standard deviation for the formation of the $FeNCS^{2+}$ ion.