

Experiment 3

Determination of an Equilibrium Constant for the Iron (III) Thiocyanate Reaction

Pre-Lab Assignment

Before coming to lab:

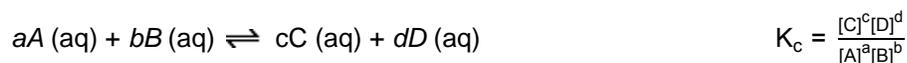
- Read the lab thoroughly.
- Answer the pre-lab questions that appear at the end of this lab exercise. The questions should be answered on a separate (new) page of your lab notebook. Be sure to show all work, round answers, and include units on all answers. Background information can be found in Chapter 15, especially sections 15.1- 15.5 in your textbook (Brown and LeMay).
- Follow the guidelines in the "Lab Notebook Policy and Format for Lab Reports" section of the lab manual to complete in your lab notebook the following sections of the report for this lab exercise: Title, Lab Purpose, Procedure and Data Tables.

Purpose

The reaction of iron (III), Fe^{3+} , with thiocyanate, SCN^- , to yield the colored product, iron (III) thiocyanate, FeSCN^{2+} , will be studied and its equilibrium constant determined using a Vernier Spectrometer. This will require that first a graph that relates the concentration FeSCN^{2+} to its absorbance be prepared. Using a different set of starting concentrations and again determining the concentration of iron (III) thiocyanate using a Vernier Spectrometer, the equilibrium constant for the reaction will then be determined.

Background

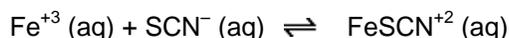
In the study of chemical reactions, chemistry students first study reactions that go to completion. You have been assuming in these familiar problems—such as calculations of theoretical yield, limiting reactants, and percent yields—that the reaction will consume *all* of one or more reactants to produce products. In fact, most reactions do not behave this way. Instead, reactions reach a state where a stable mixture of reactants and products is produced. This mixture is called the **equilibrium state**; at this point, chemical reaction occurs in both directions at equal rates. Therefore, once the equilibrium state has been reached, no further change occurs in the concentrations of reactants and products. The equilibrium constant, K , is used to quantify the equilibrium state. The expression for the equilibrium constant for a reaction is determined by examining the balanced chemical equation. For a reaction involving aqueous reactants and products, the equilibrium constant is expressed as a ratio between reactant and product concentrations, where each term is raised to the power of its reaction coefficient:



When a chemical reaction reaches equilibrium the concentrations of reactants and products no longer change with time. If one is able to measure these concentrations, the value of the equilibrium constant can be calculated.

In this laboratory you will find the equilibrium constant for the reaction:

(deep-red, orange)



Since the product, FeSCN^{2+} , has a deep red color, its concentration can be determined using spectrophotometric techniques—that is, based on how much light it is absorbing.

Once the equilibrium concentration of FeSCN^{2+} has been determined, the equilibrium concentrations of the reactants (Fe^{3+} and SCN^{-}) can be calculated. Because the stoichiometry is 1 mol Fe^{3+} : 1 mol SCN^{-} : 1 mol FeSCN^{2+} , the moles of each **reactant used up** (Fe^{3+} and SCN^{-}) in the reaction is equal to the moles of **product formed** (FeSCN^{2+}). Since you will know the initial concentrations of the reactants and the amount used up in the reaction, you will be able to subtract to find the moles of reactant remaining at equilibrium. Finally, once you know the concentration of each substance in the reaction, you can calculate the equilibrium constant, where

$$K_c = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^{-}]}$$

In this experiment you will carry out the reaction several times, each time combining different amounts of the reactants, Fe^{3+} and SCN^{-} . The experimental equilibrium constant will then be found by averaging the results from all the trials.

Before you do this, however, you will need to determine the relationship between the absorbance and molarity of $[\text{FeSCN}^{2+}]$ —a calibration curve. You will do this by measuring the absorbance of five standard solutions in which $[\text{FeSCN}^{2+}]$ is known. There is a problem here. How can you know the concentrations of FeSCN^{2+} formed in the reaction? After all, it is an equilibrium reaction so not all of the Fe^{3+} and SCN^{-} will turn into FeSCN^{2+} . In other words, unlike in Chem1A, mixing known amounts of the reactants will not necessarily yield a known amount of product.

This difficulty can be avoided using Le Chatelier's Principle. According to Le Chatelier's Principle, a reaction will shift to the right when more of a reactant is added. As more and more of the same reactant is added, more and more of the product will form. It is possible to add so much of this reactant that essentially all of the other reactant will be converted to product. You will use limiting quantities of SCN^{-} and overwhelming amounts of Fe^{3+} in the first part of the lab so that all of the SCN^{-} will be converted to FeSCN^{2+} effectively producing a known concentration. This is sometime referred to as “driving a reaction to the right”.

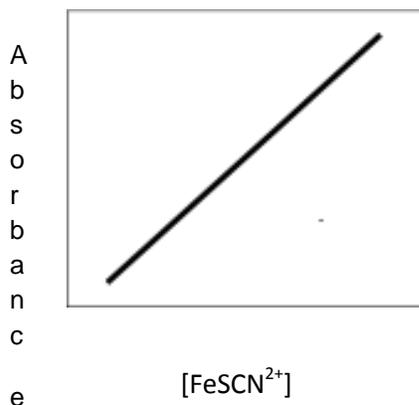


Figure 1: Plots of A vs. concentration for solutions with known concentrations of $\text{FeSCN}^{2+}(\text{aq})$ can be used as a *calibration curve*. This plot is used to determine the $\text{FeSCN}^{2+}(\text{aq})$ concentration in solutions where the value is not known.

Once your calibration curve has been prepared you will be able to prepare a series of equilibrium mixtures and determine the equilibrium constants for each trial, using your calibration graph to determine $[\text{FeSCN}^{2+}]$ and the procedure outlined above.

Procedure

SAFETY: Students must wear safety goggles at all times. The iron(III) nitrate solutions contain 1.0 M nitric acid. Nitric acid is used to prevent iron (III) from reacting with water to produce $\text{Fe}(\text{OH})_3(\text{s})$. Avoid contact with skin and eyes; wash hands frequently during the lab and wash hands and all glassware thoroughly after the experiment.

WASTE DISPOSAL: All chemicals used must go in the proper waste container for disposal.

Part A: Preparation of the Calibration Curve- the relationship between absorbance and $[\text{FeSCN}^{2+}]$

Note: The FeSCN^{2+} complex forms slowly, taking at least one minute for the color to develop. It is best to take absorbance readings after a specific amount of time has elapsed, between two and four minutes after preparing the equilibrium mixture. Do not wait much longer than four minutes to take readings, however, because the mixture is light sensitive and the FeSCN^{2+} ions will slowly decompose. You will need to plan well so that the spectrometer is calibrated and that preparation of the solutions is timed well.

1. Set up six clean, dry test tubes and number them 1–6. Mix the solutions of Fe^{3+} , SCN^- , and HNO_3 in the proportions listed below. Use a different pipet for each solution and label them so that you don't get them mixed up. **Insure that the solutions are well mixed by pouring them into a small beaker and stirring on a magnetic stir plate after preparing them in the test tube just before measuring their absorbance.**

Tube #	0.200 M $\text{Fe}(\text{NO}_3)_3$ (mL)	0.00200 M KSCN (mL)	0.1 M HNO_3 (mL)
1	5.00	0.00	5.00
2	5.00	5.00	0.00
3	5.00	4.00	1.00
4	5.00	3.00	2.00
5	5.00	2.00	3.00
6	5.00	1.00	4.00

2. Use the instructions for the Vernier Spectrometer on the following page to determine the wavelength of maximum absorbance of solution 2 (it should be close to 460 nm) and then measure the absorbance of each solution at this wavelength. **Flask 1 will be used as your blank, not distilled water however.** Record both the wavelength and each absorbance in your notebook.

Vernier SpectroVis Spectrophotometer

(Order Code: SVIS)



SpectroVis is a portable, visible light spectrophotometer.

What is Included with the SpectroVis?

- One SpectroVis unit
- 15 plastic cuvettes and lids
- One standard USB cable
- User's Guide (this document)

Software Requirements

Logger Pro 3 (version 3.6 or newer) software is required if you are using a computer. The LabQuest application version 1.1 or newer is required if you are using a LabQuest. Visit the downloads section of www.vernier.com to update your software.

Using SpectroVis with a Computer

1. Install Logger Pro 3 software (version 3.6 or newer) on your computer before using SpectroVis.
2. Connect the SpectroVis to a powered USB port or a powered hub.
3. The first time you connect a SpectroVis, your computer may ask you a few questions. Note: Do not go online for device drivers. The device drivers were installed when you installed Logger Pro 3.

Calibrate SpectroVis

1. To calibrate the SpectroVis, choose Calibrate ► Spectrometer from the Experiment menu.
2. Fill a cuvette about ¾ full with distilled water and place it in the cuvette holder.
3. Follow the instructions in the dialog box to complete the calibration, and then click .

Collect Data

There are three general types of data collection measuring absorbance – absorbance vs. wavelength, which produces a spectrum, absorbance vs. concentration for Beer's law experiments, and absorbance vs. time for kinetics experiments.

Measure the Absorbance Spectrum of an Aqueous Sample (Absorbance vs. Wavelength)

1. Fill a cuvette about ¾ full of the solution to be tested. Place the sample in the cuvette holder of the SpectroVis.

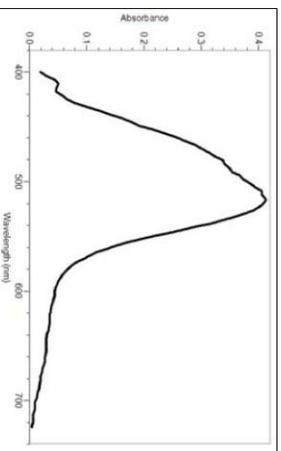


Figure 1: Typical absorbance spectrum

2. Click Collect, Click Stop to end data collection.

Conduct a Beer's Law Experiment (Absorbance vs. Concentration)

1. Measure an absorbance spectrum as described above.
2. Click on the Configure Spectrometer Data Collection button, .
3. Select Abs vs. Concentration as the collection mode. The wavelength of the maximum absorbance will be automatically selected. Click OK to continue or click Clear and select a wavelength on the graph or in the list of wavelengths.
4. Place your first Beer's law standard solution in the cuvette slot. Click Collect and then click Keep. Enter the concentration of the sample and click OK.
5. Place your second standard sample in the SpectroVis. After the absorbance readings stabilize, click Keep. Enter the concentration of the second sample and click OK.
6. Repeat Step 5 for the remaining standard samples. After you have tested the final standard, click Stop to end the data collection.
7. Click linear fit, , to see the best fit line equation for the standard solutions.
8. Place an unknown sample of solution in the cuvette holder. Choose Interpolation Calculator from the Analyze menu. A helper box will appear, displaying the absorbance and concentration of the unknown. Click OK.

Calculations for Part A

1. Calculate and record in lab notebook the $[\text{FeSCN}^{2+}]$ in each solution and its absorbance. **Because a large excess of Fe^{3+} is used, it is reasonable to assume that all of the SCN^- is converted to FeSCN^{2+} .** Be sure to take into account the dilution that occurs when the solutions are mixed. A suggested way to organize your data is below.

λ max = _____

Spectrometer Number _____

Test Tube #	0.200 M $\text{Fe}(\text{NO}_3)_3$ (mL)	0.00200 M KSCN (mL)	0.1 M HNO_3 (mL)	$[\text{Fe}^{3+}]$ after dilution	$[\text{SCN}^-]$ after dilution	$[\text{FeSCN}^{2+}]$ formed	Absorbance
1	5.00	0.00	5.00				
2	5.00	5.00	0.00				
3	5.00	4.00	1.00				
4	5.00	3.00	2.00				
5	5.00	2.00	3.00				
6	5.00	1.00	4.00				

2. Plot absorbance vs $[\text{FeSCN}^{2+}]$ using Excel, and confirm that the points fall along a straight line. Include a best-fit linear trendline, value of R^2 , and labels and units on the axis as well. In addition, because you used your blank solution to zero your spectrometer you should also select the option, "set intercept = 0," from this menu. This will cause your plot to pass through the origin. Your plot should be a perfectly straight line and your best-fit line should pass directly through each of your data points. **If any of your data points fall off of your best-fit line, you should remake that particular solution, measure its absorbance again, and replot your data using this new value until a perfectly straight line through all of your data points is obtained.**
3. Print your graph and include it in your lab report.

Part B: Determination of the Equilibrium Constant

1. Obtain six small beakers with volumes of 50 mL or 100 mL and label them 1–6.
2. Obtain about 25 mL of 0.00200 M KSCN.
3. Obtain about 30 mL of 0.00200 M $\text{Fe}(\text{NO}_3)_3$. Make sure you are using the correct concentration solution.
4. Obtain about 40 mL of 0.1 M HNO_3 .
5. Use pipets to obtain the solutions of Fe^{3+} , SCN^- , and HNO_3 in the amounts listed on the next page. Use a magnetic stir plate to insure that the solutions are well mixed. Use a different pipet for each solution, and label them so that you don't get them mixed up.

Beaker #	0.00200 M Fe(NO ₃) ₃ (mL)	0.00200 M KSCN (mL)	0.1 M HNO ₃ (mL)
1	3.00	0.00	7.00
2	3.00	2.00	5.00
3	3.00	3.00	4.00
4	3.00	4.00	3.00
5	3.00	5.00	2.00
6	3.00	6.00	1.00

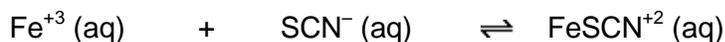
6. Measure and record the absorbance of each solution at λ_{max} found in Part A of the lab. Again, pay attention to the timing of mixing your solution. If you are doing Part B on different day than you did Part A, you will need to calibrate the spectrometer again using a blank (beaker #1).

Calculations for Part B

1. A suggested way to organize your data for Part B of the lab is below.

Beaker #	0.00200 M Fe(NO ₃) ₃ (mL)	0.00200 M KSCN (mL)	0.1 M HNO ₃ (mL)	[Fe ³⁺] after dilution	[SCN ⁻] after dilution	Absorbance
1	3.00	0.00	7.00			
2	3.00	2.00	5.00			
3	3.00	3.00	4.00			
4	3.00	4.00	3.00			
5	3.00	5.00	2.00			
6	3.00	6.00	1.00			

2. Calculate the value of the equilibrium constant the reaction from your data for each of the five equilibrium solutions (test tubes 2- 6) in Part B. You will find it helpful to organize **each** of your five calculations in an ICE table such as this one:



Initial Concentration (M)			
Change in Concentration (M)			
Equilibrium Concentration (M)			

The calculations for Part B are most easily done by following Steps 1 through 5 **in order**:

- 1: Find the initial concentrations of Fe^{3+} and SCN^- in the mixtures. You will need to account for dilutions of the stock solutions by using $M_1 V_1 = M_2 V_2$.
2. Calculate the equilibrium $[\text{FeSCN}^{2+}]$ from the measured absorbance and equation of the line on the calibration graph. Is $[\text{FeSCN}^{2+}]$ "x" or "y" on your graph?
3. Find the change in concentration of FeSCN^{2+} . Deduce the *changes* in concentration of the reactants, Fe^{3+} and SCN^- . You can do this by looking at the stoichiometry of the reaction.
4. Find the *equilibrium* concentrations of the reactants, Fe^{3+} and SCN^- .
5. Calculate K_c for the reaction for each of the mixtures by substituting values for the equilibrium concentrations of Fe^{3+} , SCN^- , and FeSCN^{2+} into the equilibrium constant expression.

The calculations for Part B can be summarized below:



	$[\text{Fe}^{3+}]$	$[\text{SCN}^-]$	$[\text{FeSCN}^{2+}]$
Initial	1. Calculated using initial concentrations and accounting for dilution	1. Calculated using initial concentrations and accounting for dilution	= 0 (why?)
Change	3. amount of Fe^{3+} reacted = amount of FeSCN^{2+} formed (why?)	3. amount of SCN^- reacted = amount of FeSCN^{2+} formed (why?)	= equilibrium value (see below)
Equilibrium	4. = Initial – Change	4. = Initial – Change	2. Determined spectrophotometrically

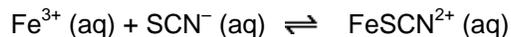
$$K_c = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} =$$

You will need to repeat these calculations for beakers 2 - 6. It is only necessary to show the work for one of the trials but be sure to have a completed ICE table for each trial in your notebook.

6. Calculate the **average** value of K_c for samples 2-6.

Post-Lab Questions

1. Does your calculated average value of K_c indicate that the equilibrium of the reaction is reactant-favored or product-favored?
2. A student does an experiment to determine the equilibrium constant for the same reaction that you will studied, but at a higher temperature.



The student mixes 5.00 mL of 2.00×10^{-3} M $\text{Fe}(\text{NO}_3)_3$ solution with 5.00 mL of 2.00×10^{-3} M KSCN solution, heats the mixture, and finds that the equilibrium concentration of FeSCN^{2+} in the mixture is 5.00×10^{-5} M. Calculate the equilibrium constant for the reaction under the conditions in this experiment

3. Using your average calculate value of K_c , calculate the concentration of FeSCN^{2+} that will form if 15 mL of 0.00150 M $\text{Fe}(\text{NO}_3)_3$ is mixed with 22 mL of 0.00100 M KSCN.

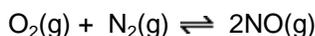
Pre-Lab Questions

1. Why will the absorbance measurements be done at a wavelength of about 460 nm? What color is 460 nm light? What color of light is being absorbed?
2. What is the purpose of diluting your samples in HNO₃ instead of water?
3. You will be varying the initial amounts of Fe³⁺ and SCN⁻ in part B. What is your hypothesis for how the equilibrium constant will vary with the trials? What is the only "variable" that can make the value of K_c change?
4. The reaction $\text{O}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ was prepared with the following initial concentrations:

$$[\text{O}_2] = 0.01 \text{ M} \quad [\text{N}_2] = 0.01 \text{ M} \quad \text{and} \quad [\text{NO}] = 0 \text{ M}.$$

At equilibrium, [NO] was measured and found to be 0.00020 M.

- a. Set-up an ICE table and calculate the equilibrium concentration for the two reactants O₂ and N₂.
 - b. Calculate K_c.
5. The same reaction is now run with the following initial concentrations:



$$[\text{O}_2] = 0.1 \text{ M} ; \quad [\text{N}_2] = 0.0001 \text{ M} ; \quad \text{and} \quad [\text{NO}] = 0 \text{ M} .$$

Because the concentration of oxygen is one thousand times as concentrated as that of nitrogen, the reaction is driven to the right effectively using up all of the N₂.

- a. Using an ICE table, calculate all the equilibrium concentrations for all species in this reaction.
- b. Do the results of your ICE show that it is a correct assumption that almost all of the N₂ placed in the vessel will be used up under these conditions?