Spectroscopic Determination of an Equilibrium Constant

GOAL AND OVERVIEW

The reaction of iron (III) with thiocyanate to yield the colored product, iron (III) thiocyanate, can be described by the following equilibrium expression.

$$Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+} \tag{1}$$

You will study this equilibrium using the Spec 20 UV-visible spectrometer. The wavelength of light absorbed most strongly by the product will be determined from the spectral profile of $FeSCN^{2+}$. A Beer's Law plot will be made for a series of $FeSCN^{2+}$ solutions of known concentration. Then, the concentrations of $FeSCN^{2+}$ will be measured spectroscopically for a set of solutions made with different initial concentrations of reactants. This data will be used to determine K_{eq}, the equilibrium constant for the reaction.

Objectives of the data analysis

- use Beer's Law to characterize amounts of molecules
- calculate solution concentrations resulting from volumetric dilutions
- understand equilibrium principles and manipulate equilibrium constant expressions
- determine equilibrium concentrations and equilibrium constants
- consider the effects of error when assumptions are used

SUGGESTED REVIEW AND EXTERNAL READING

- Reference information on spectroscopy (see Lab 9[1]) and dilutions; relevant textbook information on spectroscopy and equilibrium

BACKGROUND

This experiment investigates the equilibrium established by the reaction of the iron (III), Fe^{3+}, and the thiocyanate, SCN^-, ions. See Eq. 1. The reactants are colorless, but the $FeSCN^{2+}$ ion is orange-red colored. At equilibrium, the concentrations of these three ions must be related to each other according to the equilibrium constant expression.

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

[1] ../lab_9/manual.html

One goal in this experiment is to measure the value of K, using the spectrometer to quantitatively analyze the concentration of $FeSCN^{2+}$ ion.

Absorption spectroscopy and Beer's Law were discussed in detail and were used in the Allura Red Lab[2]. This same method will be utilized to determine $[FeSCN^{2+}]$, the colored product.

$$A = -\log(T) = \epsilon bc \tag{3}$$

$$T = \frac{\%T}{100\%} = 10^{-\epsilon bc} = 10^{-A} \tag{4}$$

Then, you will use your understanding of equilibrium processes to deduce the equilibrium concentrations of the reactants. Knowing all three concentrations listed above in Eq. 2 allows the equilibrium constant for this reaction to be calculated.

PROCEDURE

Part 1: Qualitative Observations: Is the reaction exothermic or endothermic?

1 Using a 10 mL graduated cylinder, measure out approximately 2 mL of 2×10^{-3} M $NaNO_3$ and put it in a test tube.

2 Add approximately 8 mL of 2×10^{-3} M NaSCN.

3 Add approximately 10 mL of 2×10^{-3} M $Fe(NO_3)_3$. Note the color of the solution.

4 Fill a Spec 20 cuvette no more than 2/3 full, and split the remaining solution among three test tubes.

5 Place one tube in an ice bath and one in the hot water bath on the hot plate.

6 After about 10 minutes, compare them with the solution at room temperature.

7 Discuss the implications of your observations, basing your discussion on your knowledge of Le Châtelier's principle.

Do your observations imply an *exothermic* or *endothermic* reaction?

Part 2: Spectral Profile and λ_{max} (most sensitive wavelength) of $FeSCN^{2+}$

1 Measure transmittance ($\%T$) to 0.1% of the mixtures in your cuvette in the range from 370 to 560 nm.

- **a** Use a cuvette containing 2×10^{-3} M $NaNO_3$ as a blank to set 100% transmission.
- **b** Check the $\%T$ readings at 20 nm intervals.
- **c** When you reach the region of minimum transmittance, reduce the intervals to 10 or even to 5 nm.

[2] ../lab_9/manual.html

2 For the wavelength of minimum $\%T$, calculate the absorbance, A, of the solution ($A = -\log\ T$) to the appropriate number of significant figures.

3 Identify the wavelength of maximum absorbance, the experimental value of λ_{max}.

How does your λ_{max} compare with your answer to Question 1 of the pre-lab assignment?

4 Set your spectrometer to λ_{max} for parts 3 and 4.

Part 3: Beer's Law Curve for $FeSCN^{2+}$: determining ϵ of the product at λ_{max}

To make solutions of known concentrations of $FeSCN^{2+}$, you cannot simply dissolve a salt containing $FeSCN^{2+}$ in water because the ion will dissociate in order to satisfy the equilibrium constant expression.

If K_{eq} were known, solutions with known initial concentrations of $FeSCN^{2+}$ could be made, and algebra could be used to find equilibrium concentrations of Fe^{3+}, SCN^-, and $FeSCN^{2+}$. However, K is what you are trying to find in Part 4.

In order to overcome this difficulty, you will take spectral data for a set of solutions made by mixing a very high Fe^{3+} concentration with extremely small SCN^- concentrations. Assume that SCN^- is the limiting reactant (i.e., that essentially all of it is used up to make $FeSCN^{2+}$). By doing this, you can *equate* the *equilibrium concentration of iron (III) thiocyanate*, $[FeSCN^{2+}]_{eq}$ to the *initial concentration of thiocyanate*, $[SCN^-]_{\text{initial}}$.

Once you have actually determined K_{eq}, you must *return to this assumption and verify its validity.*

Note for Parts 3 & 4: You may wish to split the dilution work with your partner to save time. One person could do Part 3 while the other is doing Part 4.

1 Take about 100 mL of 0.1 M Fe^{3+} solution (***solution B***) in a small labeled beaker.

2 Make the strongest colored solution of NaSCN and $Fe(NO_3)_3$ (***solution A***).

- **a** Using a volumetric pipet, put 5 mL of 2×10^{-3} M NaSCN (concentration known to 1%) into a 50 mL volumetric flask.
- **b** Fill to the mark with solution B (above; 0.1 M Fe^{3+} solution).

3 Use only volumetric glassware, not graduated pipets or cylinders.

- You have the following volumetric pipets available: 1, 2, 5, 10 mL.
- You have the following volumetric flasks available: 10, 50, 100 mL.

Accurately create 10 mL volumes of the following dilutions of solution A with solution B. As each of these solutions is created, measure its $\%T$ to 0.1%.

- **a** Pure B for use as a blank (faint straw-colored, no colored complex); this is 0.1 M $Fe(NO_3)_3$.
- **b** 1 mL A into 10 mL flask, filled to mark with B
- **c** 3 mL A into 10 mL flask, filled to mark with B

d 5 mL A into 10 mL flask, filled to mark with B

e 7 mL A into 10 mL flask, filled to mark with B

f 9 mL A into 10 mL flask, filled to mark with B

g Pure A, the pure, most red-orange solution

4 Calculate absorbance for each solution: $A = –\log(\%T/100\%)$.

5 Make a Beer's Law plot of absorption versus concentration of $FeSCN^{2+}$ (A vs $[FeSCN^{2+}]$) for these 7 points. Use two significant figures in your concentration values and three for your absorbance values.

6 Draw the best-fit straight line to the points.

7 This best-fit line mathematically has the form of Beer's Law: $A = \epsilon bc$, with slope $= \epsilon b$ and y-intercept $= 0$; $\epsilon =$ molar extinction coefficient in L/mol · cm, $b =$ pathlength in cm, and $c =$ concentration in mol/L. Determine the slope to the ones place.

8 Using the *measured* pathlength b of your cuvette (to 0.01 cm) and your slope, calculate the value of the extinction coefficient for $FeSCN^{2+}$ at its λ_{max} to the ones place.

9 Record which Spec 20 you used so you can use the same one for Part 4.

Summary of Desired Quantities Parts 1 – 3.

- Temperature Dependence: Is the reaction exothermic or endothermic? Explain.
- Spectral Profile: What is λ_{max}?
- Beer's Law Plot: Graph of Absorbance versus $[FeSCN^{2+}]$ noting ϵ at λ_{max}.

Part 4: Equilibrium Constant for the Formation of $FeSCN^{2+}$

In this part of the experiment, you will prepare five solutions with the same initial concentration of Fe^{3+} ion but different initial concentrations of SCN^- ion. As you make each solution, measure its percent transmittance at λ_{max} (Part 2) and use your Beer's Law plot (Part 3) to establish the equilibrium $FeSCN^{2+}$ concentration. From the initial concentrations of the reactants and the equilibrium concentration of the product, you can calculate the experimental value of K_{eq} for each of the five solutions using Eq. 2.

1 Use the solutions provided, each of which is 2×10^{-3} M: NaSCN, $Fe(NO_3)_3$, and $NaNO_3$.

2 Use volumetric pipets and a 10 mL volumetric flask to prepare each of the following five solutions.

- NaSCN and $Fe(NO_3)_3$ deliver SCN^- and Fe^{3+} to the solution.
- $NaNO_3$ is used to fill the flask to 10 mL.
- The "Total used" row is designed to help you estimate how much of the stock solutions you should take in labeled beakers to your lab station.
- Please minimize waste – do not take extra and please share leftovers.

Trial	2×10^{-3} M NaSCN	2×10^{-3} M $Fe(NO_3)_3$	2×10^{-3} M $NaNO_3$
blank	0 mL	5 mL	5 mL (blank)
1	1 mL	5 mL	4 mL
2	2 mL	5 mL	3 mL
3	3 mL	5 mL	2 mL
4	4 mL	5 mL	1 mL
5	5 mL	5 mL	0 mL
Total used	15 mL	30 mL	15 mL

Waste disposal: The solutions must be put into the labeled waste bottles in the back hood. Nothing can go down the sink.
If you are ever in doubt, ask your TA.

3 Find equilibrium concentrations of Fe^{3+}, SCN^{-}, and $FeSCN^{2+}$ to two significant figures. (See Equations 1 and 2.)

ICE tables will help you determine these values. Initial amounts, changes in amounts, and final equilibrium amounts are shown. These values must be in moles/L.

	Fe^{3+} +	SCN^{-} ⇆	$FeSCN^{2+}$
I_nitial amount (mol/L)	$[Fe^{3+}]_{initial} = M_1V_1/V_2$	$[SCN^{-}]_{initial} = M_1V_1/V_2$	0
C_hange in amount (mol/L)	$-x$	$-x$	$+x$
E_quilibrium amount (mol/L)	$[Fe^{3+}]_{initial} - x$	$[SCN^{-}]_{initial} - x$	$x = A/slope$

- **initial amounts of reactants** (amounts before the reaction begins): determined using the dilution equation
  - To find the initial concentration of SCN^{-}, use the dilution equation: $(M_1V_1)/V_2 = M_2$, where $V_2 = 10$ mL.
  - To find the initial concentration of Fe^{3+}, use the dilution equation: $(M_1V_1)/V_2 = M_2$, where $V_2 = 10$ mL.
- **initial amount of product** (the amount before the reaction begins): zero
- **equilibrium concentration of product** ($[FeSCN^{2+}]_{eq}$) : determined spectroscopically

$[FeSCN^{2+}]$ at equilibrium is determined using Beer's Law; x is the amount of $FeSCN^{2+}$ created (determined experimentally).

$$x = [FeSCN^{2+}]_{eq} = \frac{A}{\epsilon b} = A/\text{slope} \tag{5}$$

To complete your ICE tables, one for each trial in Part 4 (concentrations should have two significant figures):

a Begin by filling out the product column from the bottom up. Because the stoichiometry is 1:1:1, the amount of reactant consumed is equal to the amount of product formed.

b Fill in the rest of the ICE table box-by-box until the equilibrium reactant concentrations are determined.

4 Use Eq. 2 and the equilibrium concentrations from the bottom row of each ICE table to calculate K_{eq} to two significant figures for the five trials in Part 4.

5 Find the average value of K_{eq}, the standard deviation, and the relative error (standard deviation divided by the average).

Are the values of K for all trials similar? Should they be?

Assumption Check Used in Making Beer's Law Plot

Given your value of K, go back and check the validity of the assumption you made in Part 3.

1 Rewrite Eq. 2 so that the ratio of $[FeSCN^{2+}]_{\text{eq}}$ to $[SCN^{-}]_{\text{eq}}$, $[FeSCN^{2+}]_{\text{eq}}/[SCN^{-}]_{\text{eq}}$, is on one side.

2 Calculate the approximate ratio of $[FeSCN^{2+}]_{\text{eq}}/[SCN^{-}]_{\text{eq}}$ using K_{eq} and $[Fe^{3+}]$. Use your average value for K_{eq}. The Fe^{3+} concentration was approximately 0.1 M in Part 3; the change in its concentration should have been negligible.

3 The assumption that essentially all of the SCN^{-} reacted to form $FeSCN^{2+}$ would mean that this ratio would need to be large. **Is it?**

If the ratio is small, the assumption was clearly a bad one and the experiment is useless in determining the equilibrium $FeSCN^{2+}$ concentration and K_{eq}. At least 95% of the initial SCN^{-} should react to form $FeSCN^{2+}$ at equilibrium.

4 Discuss how good the assumption was and how the assumption affected the calculated values of K_{eq}.

- For example, if K_{eq} is 350, then $[FeSCN^{2+}]_{\text{eq}}/[SCN^{-}]_{\text{eq}} \approx 35$.
- This means that 35 out of 36 SCN^{-} initially present have been converted to $FeSCN^{2+}$ at equilibrium; 1 out of 36 is present as SCN^{-}.
- That is about a 3% error in the $FeSCN^{2+}$ concentration due to just the assumption.
- And, $[FeSCN^{2+}]_{\text{eq}}$ is used to determine the other values at equilibrium; 3% error in concentrations translates into roughly 9% error in K_{eq} (again, this is just from the assumption and does not consider other experimental variables).

5 Checking the assumption is only part of a thorough experimental analysis; it should not be considered the main point of the lab.

RESULTS

Complete your lab summary or write a report (as instructed).

Abstract

Results

Observations for Part 1

λ_{max} and absorbance at λ_{max} for Part 2

Beer's Law plot for Part 3 including slope(ϵb)

Ice tables, individual and average K_{eq} values

Sample Calculations

Absorbance from transmittance

Concentration calculations

K_{eq} calculation

Assumption testing

Discussion/Conclusions

What you found out and how

Relating results to predictions/theory

How was Part 3 dependent on Part 2?

Validity of the assumption

What can you conclude from this experiment

Review Questions

