# 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 and Science Skills

- Perform volumetric dilutions and calculate resulting molarities.

- Understand and explain absorption spectroscopy and the mathematical relationships between percent transmittance, absorbance, concentration, path length, and extinction coefficient.

- Apply linear fitting methods to find relationships between dependent and independent variables, such as percent transmittance (absorbance) and concentration.

- Explain and apply Beer's Law; describe the assumptions and limitations imposed by the nature of the equilibrium on the calculation of $FeSCN^{2+}$ associated with the absorption data.

- Use absorption data to qualitatively and quantitatively analyze the concentration of $FeSCN^{2+}$ in solution.

- Identify and discuss factors or effects that may contribute to the uncertainties in values or assessments made from experimental data.

- Analyze, quantify, and discuss the uncertainty in results 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

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[1] ../lab_9/manual.html

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.

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

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 $2 \times 10^{-3}$ M $NaNO_3$ and put it in a test tube.

**2** Add approximately 8 mL of $2 \times 10^{-3}$ M NaSCN.

**3** Add approximately 10 mL of $2 \times 10^{-3}$ 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 $\lambda_{\mathbf{max}}$ (most sensitive wavelength) of $\mathbf{FeSCN^{2+}}$

**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 $2 \times 10^{-3}$ 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.

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[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 $\lambda_{\text{max}}$.

How does your $\lambda_{\text{max}}$ compare with your answer to Question 1 of the pre-lab assignment?

**4** Set your spectrometer to $\lambda_{\text{max}}$ for parts 3 and 4.

## Part 3: Beer's Law Curve for FeSCN²⁺: determining $\epsilon$ of the product at $\lambda_{\text{max}}$

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 $K_{\text{eq}}$ 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*, $[FeSCN^{2+}]_{\text{eq}}$ to the *initial concentration of thiocyanate*, $[SCN^-]_{\text{initial}}$.

Once you have actually determined $K_{\text{eq}}$, 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 $2 \times 10^{-3}$ 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 $\lambda_{\max}$ 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 $\lambda_{\max}$?

- Beer's Law Plot: Graph of Absorbance versus $[FeSCN^{2+}]$ noting $\epsilon$ at $\lambda_{\max}$.

## 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 $\lambda_{\max}$ (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 $2 \times 10^{-3}$ 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(NO₃)₃ | 2×10⁻³ M NaNO₃ |
|---|---|---|---|
| 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).

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

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 $[FeSCN^{2+}]_{eq}$ to $[SCN^-]_{eq}$, $[FeSCN^{2+}]_{eq}/[SCN^-]_{eq}$, is on one side.

**2** Calculate the approximate ratio of $[FeSCN^{2+}]_{eq}/[SCN^-]_{eq}$ 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 $[FeSCN^{2+}]_{eq}/[SCN^-]_{eq} \approx 35$.

- 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, $[FeSCN^{2+}]_{eq}$ 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

$\lambda_{\text{max}}$ and absorbance at $\lambda_{\text{max}}$ for Part 2

Beer's Law plot for Part 3 including slope($\epsilon b$)

Ice tables, individual and average $K_{\text{eq}}$ values

## Sample Calculations

Absorbance from transmittance

Concentration calculations

$K_{\text{eq}}$ 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