

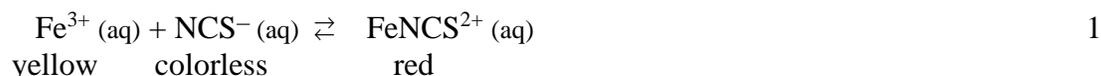
Laboratory 2: The Equilibrium Constant for the Formation of the Iron(III) Thiocyanate Complex

Reading: Olmstead and Williams, *Chemistry*, Chapter 14 (all sections)

Purpose: The equilibrium constant for the reaction $\text{Fe}^{3+}(\text{aq}) + \text{NCS}^{-}(\text{aq}) \rightleftharpoons \text{FeNCS}^{2+}(\text{aq})$ is determined.

Introduction

The Iron(III)-Thiocyanate Equilibrium This experiment is based on the same reaction that was studied last week:



The solution also contains the ions K^{+} and NO_3^{-} , but these are spectator ions and do not participate in this reaction. Quantitatively, the relative amounts of the two reactants and the product are related by the equilibrium constant of the reaction; in this case, the formation constant K_f :

$$K_f = \frac{[\text{FeNCS}^{2+}]_{\text{eq}}}{[\text{Fe}^{3+}]_{\text{eq}} [\text{NCS}^{-}]_{\text{eq}}} \quad 2$$

K_f can be calculated through an experimental determination of the equilibrium concentration of the complex, $[\text{FeNCS}^{2+}]_{\text{eq}}$, in equilibrium with $[\text{Fe}^{3+}]_{\text{eq}}$ and $[\text{NCS}^{-}]_{\text{eq}}$. You will use a *standard curve* to determine $[\text{FeNCS}^{2+}]_{\text{eq}}$. The equilibrium concentrations of the other two ions is determined using the 1:1 stoichiometry of the reaction:

$$[\text{Fe}^{3+}] = [\text{Fe}^{3+}]_o - [\text{FeNCS}^{2+}]_{\text{eq}} \quad 3$$

$$[\text{NCS}^{-}] = [\text{NCS}^{-}]_o - [\text{FeNCS}^{2+}]_{\text{eq}} \quad 4$$

Where $[\text{Fe}^{3+}]_o$ and $[\text{NCS}^{-}]_o$ are the initial, analytical, concentrations.

Use of the Standard Curve

Use of a standard curve is a common experimental strategy in chemistry to determine the concentration of an unknown solution. In this technique, a series of solutions with known concentrations is prepared and then the absorbance of each standard solution is measured. The absorbance is then plotted versus concentration to yield the standard curve, which is often a straight line with some scatter caused by experimental error. Regression analysis of the data using the method of least squares allows determination of the best fit line. Curve fitting is easily accomplished with Excel, which not only provides the equation of the best-fit line but also provides information as to the quality of the straight line with a regression coefficient, R^2 . The R^2 value ranges from 0 to 1.0, with 1.0 indicating a perfect fit. Subsequent measurement of the absorbance in an unknown sample allows determination of the unknown concentration through the equation of the standard curve.

The standard curve that you will generate is based on the red color of the FeNCS^{2+} ion. You will make up a series of solutions containing known amounts of this chromophore (a substance that absorbs light) and use Beer's Law to relate the resulting experimentally determined values of

absorbance to the known concentrations. Beer's law has many forms, the most common of which is $A = \epsilon lc$, where A is the absorbance, ϵ is the molar absorption coefficient in $\text{mol}^{-1} \text{L cm}^{-1}$, l is the path length of the cuvette in cm, and c is the concentration in mol L^{-1} . The slope of the plot of absorbance vs. concentration is the molar absorption coefficient.

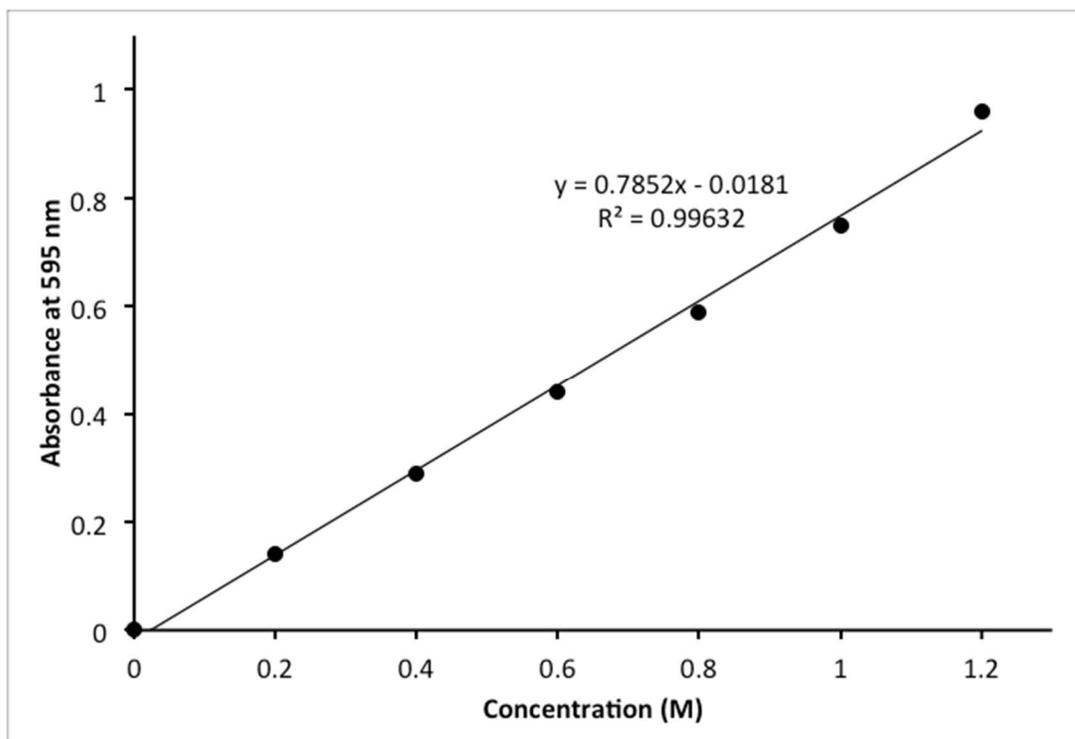


Figure 1: A typical standard curve based on Beer's Law. Beer's Law is considered to be most reliable for absorbance values between 0.1 and 1. Unknown concentrations of a given molecule can be determined using the equation of the linear trend line. Use the (0,0) point in the curve fit.

To determine the standard curve, the concentration of FeNCS^{2+} in a series of solutions must be accurately known. The concentration of FeNCS^{2+} in a solution can be calculated using the formation constant, K_f . However, the formation constant is not known. Rather, the purpose of this experiment is to calculate the formation constant, which leaves us in a bit of a quandary. How can we create a series of solutions of known FeNCS^{2+} concentrations without knowing the equilibrium constant? We can use our knowledge of LeChatelier's principle to determine how to force the equilibrium position essentially to completion, so that the stoichiometry of the reaction alone can be used to find the concentrations of FeNCS^{2+} . Consider the equilibrium, reaction 1:



What stress can we apply to force the equilibrium very far to the right, while maintaining either Fe^{3+} or NCS^{-} as the limiting reagent? For example, assume NCS^{-} is the limiting reagent with initial concentration $[\text{NCS}^{-}]_0$. If the equilibrium lies very far to the right, then $[\text{FeNCS}^{2+}]_{\text{eq}} = [\text{NCS}^{-}]_0$, because of the 1:1 stoichiometry.

Experimental Procedure

You will be measuring the absorbance of the thiocyanate equilibrium with a spectrophotometer. For this type of quantitative analysis, you need to be as exact as possible about the volumes that you measure. You will use 10.00 mL volumetric flasks to make up your solutions. With a volumetric flask you bring the total volume up to the white line to achieve a very accurate final volume. You will use automatic micropipettors to deliver the reagents into the volumetric flask. Leave the micropipettors set to 500 μL for this experiment and just make multiple additions to reach 1 mL, 1.5 mL, etc. **If you have any questions about the micropipettors, please ask your instructor or student assistant before use.** Micropipettors can be severely damaged if they are incorrectly used.

A. Determination of the Wavelength of Maximum Absorbance of the FeNCS^{2+} Ion

You will establish a standard curve to calibrate the absorbance-concentration dependence of the FeNCS^{2+} complex ion, but first you will need to determine the wavelength of maximum absorbance of the chromophore using the SpectroVis Plus diode-array spectrophotometers. The SpectroVis Plus instructions will be available in the laboratory.

1. Using a 10-mL volumetric flask, prepare 10.00 mL of an iron-thiocyanate solution containing 1.00 mL of 0.200 M $\text{Fe}(\text{NO}_3)_3$ and 2.00 mL of 0.00200 M KNCS. Use the micropipettes to measure these volumes. Then carefully add enough deionized H_2O to bring the final volume to the calibration line on the flask. Fill a cuvette three-quarters full with this solution. Be sure to wipe the cuvette with a Kimwipe to remove fingerprints and solution droplets.
2. Calibrate the spectrophotometer using 0.200 M $\text{Fe}(\text{NO}_3)_3$ alone as the reference solution in its own cuvette. For each subsequent determination, the spectrum of the reference solution is subtracted from the sample spectrum. Through this calibration process, the reference spectrum accounts for any background absorption that is not related to the chromophore that is being determined.
3. Replace the reference cuvette with the cuvette containing the iron-thiocyanate solution. Determine the wavelength of maximum absorbance, λ_{max} , and use this wavelength in subsequent absorbance measurements. If the peak has an absorbance that is greater than about 2, the peak may be somewhat flattened or “off-scale.” In this case, it is difficult to determine λ_{max} exactly. You should therefore dilute the solution with water until the absorbance reading is on scale. Record the absorbance reading; you can use this value as one of the data points for your standard curve.

B. Generation of the Standard Curve

For a good standard curve, the absorbance readings should be in the range of about 0.1 to 1.5 (an absorbance of 2 corresponds to 99% of the light being absorbed, which is at the upper limit of what can be measured accurately). You will select an appropriate range of FeNCS^{2+} concentrations based on your observations from the previous section. You will use a large excess of Fe^{3+} ion, which will drive the reaction to completion, with NCS^- as the limiting reagent. (Note that the $\text{Fe}(\text{NO}_3)_3$ solution is made up to include HNO_3 at a final concentration of 0.0100 M to prevent the formation of other iron complexes that may exist in the presence of base, but you do not have to account for this addition in any of your calculations.)

1. Prepare *five more* solutions in 10-mL volumetric flasks containing varying concentrations of FeNCS^{2+} in a total final volume of 10.00 mL. Each solution should contain 1.00 mL of 0.200 M $\text{Fe}(\text{NO}_3)_3$ and known, varying amounts of 0.00200 M KNCS. Add water to bring the final volume to 10.00 mL in each case. We recommend that in all cases your final concentration of KNCS is no higher than 0.8×10^{-3} M, or the sample is likely to have an absorbance reading greater than 1.5. (*You should calculate the volume of added 0.00200 M KNCS that gives a final concentration of 0.8×10^{-3} M in your laboratory notebook*).
2. Take the absorbance at the wavelength determined in **Part A** of each of the solutions. If the absorbance readings are not within appropriate limits, make up more solutions until you have at least six concentrations that are within the 0.01 – 1.5 absorbance range.
3. Construct a standard curve as described in the **Data Analysis** section.

C. Determination of the K_f

You will now make solutions containing constant amounts of Fe^{3+} and varying amounts of NCS^- and use the standard curve to determine the equilibrium FeNCS^{2+} concentrations based on the measured absorbance. The equilibrium concentrations are used to calculate K_f .

1. Mix five combinations of Fe^{3+} and NCS^- each in a total final volume of 10.00 mL. For each, use 5.00 mL of **0.00200 M** $\text{Fe}(\text{NO}_3)_3$ [this is a different solution than the one used above!], and known, varying amounts of the 0.00200 M KNCS, making up the total volume with water. Record the laboratory temperature; equilibrium constants are temperature dependent.
2. Determine the absorbance of the FeNCS^{2+} complex ion for each solution after recalibrating appropriately (Caution: what should the reference solution be this time? Think carefully!). Use the standard curve generated in **Part B** to convert the absorbance values into concentrations, $[\text{FeNCS}^{2+}]_{\text{eq}}$. Remember that your absorbance values should fall between the minimum and maximum absorbance values on the standard curve for best accuracy. If some of your trials are off the standard curve, make new solutions until you have five good trials within the standard curve.

Data Analysis

1. In Excel, construct a standard curve of absorbance versus $[\text{FeNCS}^{2+}]$ (mol/L) for your standard solutions from **Part B**. Remember for plots in Excel the first data column corresponds to X and the second corresponds to Y; thus, your first column should be concentration, not absorbance. Note that [0, 0] should be included as a data point. Determine the equation of the best-fit line and the R^2 value. Use the linest function to determine the standard deviation of the slope and intercept. An example of the output of the linest function is shown below with labels for the fit values that are determined (see the Error Analysis handout):

slope	12443.7	42.483	intercept
\pm	123.38	0.389	\pm
R^2	0.9997	0.0387	st.dev.y
F	10171.6	3.00	df
SS _{reg}	15.2657	0.0045	SS _{resid}

In this example, the slope is 12443.7 ± 123 and the intercept is 42.48 ± 0.39 . In this example, the slope is known to 3 significant figures and the intercept is known to 2 significant figures. (For other examples, 123.4 ± 1.4 has three significant figures, while 123.4 ± 14.0 has only two

significant figures.) The correlation coefficient, R^2 , is 0.9997. Make sure that you include a copy of your standard curve both in your report and your notebook.

2. From the standard curve, calculate the $[\text{FeNCS}^{2+}]_{\text{eq}}$ for each of your trials of **Part C**.
3. Use the stoichiometry of the FeNCS^{2+} complex ion formation to determine how much of each reactant was consumed and what the corresponding equilibrium concentrations of Fe^{3+} and NCS^- for your five trials of **Part C**.
4. Use the equilibrium values, $[\text{Fe}^{3+}]_{\text{eq}}$, $[\text{NCS}^-]_{\text{eq}}$, and $[\text{FeNCS}^{2+}]_{\text{eq}}$ to calculate K_f using equation 2 for each of your solutions. Calculate an average K_f , and the standard deviation for your trials of **Part C**. Determine the number of significant figures in the final equilibrium constant. You may wish to refer to the Error Analysis hand out and the Error Analysis Example on the lab Web page for information on standard deviation, and random and systematic error.

LABORATORY REPORT: Use the Report form for this experiment.

Use complete sentences, the proper number of significant figures, and include units. Equations, reactions, tables, and diagrams can be written by hand. The sections of your report are:

Introduction (2-sentence maximum): State the scientific purpose of the experiment. Describe the method you will use, in a general sense. Do not discuss the experimental procedure details or data analysis steps. Don't include pedagogical goals (e.g to teach us how to use.....).

Procedure: Give a one to two sentence description of the general procedure used to determine the equilibrium constant. Reference the lab write-up on the CH142 On-line Laboratory Manual and list any changes. Give the cell material and path length and the manufacturer and model of the spectrophotometer.

Results: Give the concentrations of the stock Fe^{3+} and NCS^- solution that you used for preparing the standard curve (provided for you in the laboratory). Give the concentration of Fe^{3+} in the standard solutions. Give the concentrations and absorbances used to construct the standard curve as Table 1:

Table 1: *add a caption.*

$[\text{NCS}^-]_0$ (M)	$[\text{FeNCS}^{2+}]_0$ (M)	Absorbance
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Notice that tables in lab reports should not look like Excel spreadsheets with every cell outlined. Report the slope and intercept of the curve fit, including the uncertainty of the slope and intercept. Report the molar absorption coefficient and corresponding standard deviation. Attach a copy of the standard curve plot. Make sure the axes are labeled.

Give the temperature of the equilibrium constant determination. Give the initial concentration, absorbance, equilibrium concentrations and corresponding formation constant for each

equilibrium constant determination in Table 2:

Table 2: *add a caption.*

$[\text{NCS}^-]_o$ (M)	Absorbance	$[\text{FeNCS}^{2+}]_{\text{eq}}$ (M)	$[\text{Fe}^{3+}]_{\text{eq}}$ (M)	$[\text{NCS}^-]_{\text{eq}}$ (M)	K_f
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Report the average and standard deviation of the formation constants. Mention any student errors that may have caused problems in the determinations. All tables and plots should have a table or figure number and a caption. Refer to this Table or Figure with an explicit reference (e.g. see Figure 2) in the text of this section.

Discussion:

- (a). Purpose accomplished: Restate the purpose of the experiment, but as a completed goal.
- (b). Write the reaction that you are studying.
- (c). Give the molar absorption coefficient and the standard deviation from the standard curve fit. Report the corresponding number of significant figures in the molar absorption coefficient.
- (d). Give the average and standard deviation of the trials for the equilibrium constant. Report the corresponding number of significant figures in the equilibrium constant.
- (e). Consider the effect of random and systematic errors.
 - (i). *Consider random error by comparing the expected and observed uncertainty in the final result:* Reference to the table of uncertainties in the “Error Analysis Example” on the lab Web page shows that the volumes and absorbances in this exercise should be known to three significant figures or better. If the measurements are known to three significant figures, then the molar absorption coefficient and the equilibrium constant should be known to roughly three significant figures. Compare the number of significant figures of the measurements to the number of significant figures in the equilibrium constant. There are two possibilities for this comparison (choose one and include the corresponding statement in your discussion):
 - (1). If the number of significant figures in the measurements is the same as the number of significant figures in the equilibrium constant then state: “The uncertainty of the measurements is the same as the uncertainty of the observed equilibrium constant, showing that the random error in the final result is consistent with the expected random error in the measurements.”
 - (2). If the number of significant figures in the measurements is less than the number of significant figures in equilibrium constant then state: “The uncertainty of the measurements is less than the uncertainty in the observed equilibrium constant, showing that an additional source of random error is present in the uncertainty of the final result.”
 - (ii). *Consider systematic error:* Suggest one source of systematic error for the standard curve. Remember that student mistakes are neither random nor systematic errors; student mistakes are just student mistakes. Some possible sources of systematic error are errors in the concentrations of the supplied $\text{Fe}(\text{NO}_3)_3$ or KNCS stock reagents, the calibrated volume of the micropipettor, or the calibration of the spectrophotometer. What effect does the source of

systematic error have on the standard curve? (For example, does the systematic error cause curvature in the standard curve or increase or decrease the value determined for the molar absorption constant?)

- (f). To summarize the experiment answer the following question: Note that the initial conditions for the different equilibrium measurements vary significantly in your report Table 2. Observe the values for the individual formation constants. Use the data in Table 2 to explain, in words in a general sense, the relationship between the initial conditions and the formation constant. In other words, what is the meaning of an equilibrium constant?

Literature Cited: Give all literature cited, numbered according to the references in the body of your report. See the format for the literature reference to the lab manual given in last week's report.

Attach the standard curve. Attach your data tables if they are not included in the bulk of the Report.