Matter and Motion Winter 2016
Lab 3: Determining an Equilibrium Constant
Adapted from P. Pessiki, The Evergreen State College

Purpose: The equilibrium constant for the formation of $[FeNCS(H_2O)_5]^{2+}$ from iron (III) nitrate and potassium thiocyanate is to be experimentally determined. Absorption spectroscopy will be used to measure the concentration of $[FeNCS(H_2O)_5]^{2+}$.

Introduction: In chemistry we can quantify equilibrium through the equilibrium constant. From the textbook we see how to crunch the numbers in different ways if we are given the data. In this lab, we will make the measurements and obtain our own data and then crunch the numbers.

Quantifying the change in the concentration of a reactant or product is necessary in this experiment. In the experiment today, the reaction establishes equilibrium in a short period of time, as is often the case when doing solution chemistry. We are *not* measuring the rate of this reaction. We are only going to measure the final concentration of the products. From this measurement, calculations can be performed.

In this experiment, absorption spectroscopy is utilized to measure the concentration of the product of this reaction, $[FeNCS(H_2O)_5]^{2+}$. This reaction is shown below and in Figure 1. Pay attention to charges. The oxidation state of the iron ion is not changing. Note the spectator potassium is not shown.

$$[Fe(H_2O)_6]^{3+} + SCN^- \leftrightarrow [FeNCS(H_2O)_5]^{2+} + H_2O$$

The details of the absorption spectroscopy technique will be reviewed in a pre-lab lecture and can also be reviewed in the background info of our Beer's Law lab from fall quarter. In short, we are making use of the equation $A = \varepsilon \cdot C \cdot l$ where C is the concentration, which we know because we made the solutions (**check the labeled concentrations!**), l is the path length of our spectrophotometric cell (one cm), A is the absorbance, which we measure, and ε is the "molar absorptivity" which we will determine from our Beer's Law Plot.

This lab involves transition metal chemistry with the *d electrons* of the iron (III) ion. In water it is best to think of Fe^{3+} as the $[Fe(H_2O)_6]^{3+}$ ion. In an aqueous solution the water molecules from solution are constantly exchanging with the bound water molecules (through the oxygen of the water, see FIGURE 1, below). The water molecules can be easily replaced by other molecules, hence and avenue for chemistry.

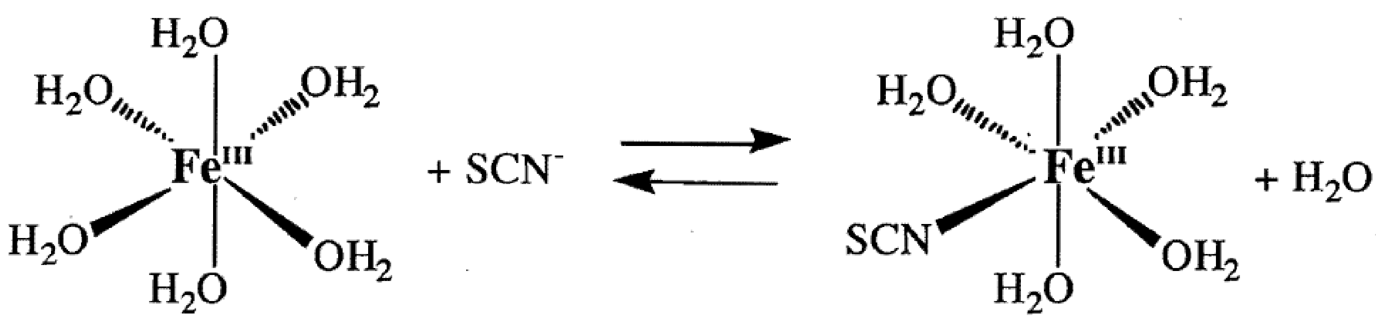


Figure 1. The reaction between thiocyanate and iron (III) nitrate to form the isothiocyanatoiron (III) ion.

A typical reaction that the hex-aqua iron (III) ion undergoes is shown in FIGURE 2. It delivers up a proton readily. To avoid this reaction, all reaction in this lab will be done in 0.1 M nitric acid, HNO_3. This forces the bound waters to remain protonated. The pK_a of the reaction shown below is about 3.1. Note the charges on the iron complexes; this is acid-base chemistry, *not* redox chemistry.

$[Fe(H_2O)_6]^{3+} \leftrightarrow [FeOH(H_2O)_5]^{2+} + H^+$

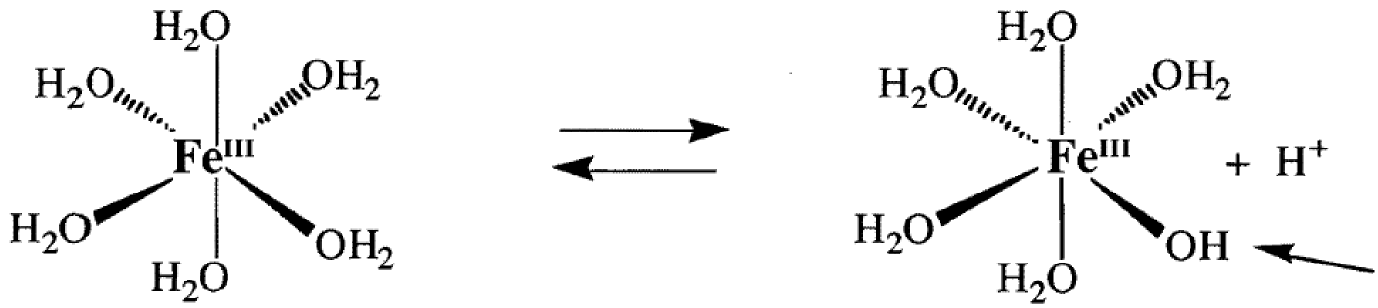
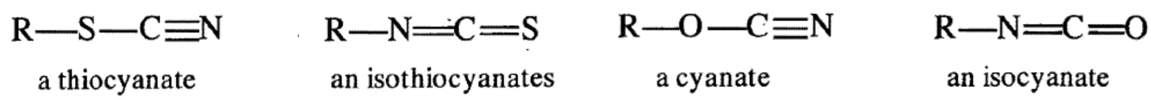


Figure 2. The ionization of the $[Fe(H_2O)_6]^{3+}$ species.

Lastly, the groups around the central metal atom are called "ligands." The ligand we are dealing with in this lab is thiocyanate (see Fig. 1). It is an ion with a negative one charge. Shown below is summary of the nomenclature of organic cyanates, thiocyanates, and their *iso*-derivatives. Note the 'R' is simply a place holder representing the rest of the molecule.



Prelab

Read the lab carefully (including Postlab!) and then complete the Prelab before coming to lab.

1. Some of the words in this lab may be new to you. Make a list of any new vocabulary and their definitions.
2. Write the full electron configuration of the Fe^{3+} ion.
3. What question is Part III of this lab looking to answer? Create a hypothesis regarding the outcome of this experiment. Be sure to justify your hypothesis with some theory.
4. Identify any parts of the lab that are unclear to you (what to do for a certain step, the purpose of a certain step, how to answer a Postlab question etc…) and come prepared to lab with questions about these parts.

Procedure

The purpose of this experiment is to measure the equilibrium constant for the following reaction: $Fe^{3+} + SCN^- \leftrightarrow [FeNCS]^{2+}$. In Part I of the lab we will make a plot of absorbance (A) versus $[FeNCS]^{2+}$ concentration. As you may recall from fall quarter, this plot is known as a Beer's Law plot. Our measurements will be made at a wavelength of about λ=448 nm, the exact value to be determined.

In the second part of the experiment, solutions containing a mixture of the two reactants (Fe^{3+} & SCN^-) at various concentrations will be prepared. The concentration of $[FeNCS]^{2+}$ will be determined using the Beer's Law plot obtained above. From this, all other species concentrations can be determined and the equilibrium constant can be calculated.

Part I: Beer's Law Plot

In Part I, the epsilon value, ε (as discussed above) for $[FeNCS]^{2+}$ will be determined at a wavelength near λ=448 nm (look for the maximum absorbance and record there). A Beer's Law plot will then be constructed. The strategy is to use an excess of the Fe^{3+} ion so we can conclude that the concentration of $[FeNCS]^{2+}$ will equal the starting concentration of thiocyanate ion. This is a fair assumption considering the strong attraction between the thiocyanate ion and the Fe^{3+} ion, coupled with proper reaction conditions. **Table 1** shows the amounts of reagents needed for the Beer's Law plot. The sequence of addition I suggest is as follows: first some dilute nitric acid, then the Fe^{3+} ion, followed by the KSCN, followed by the remainder of dilute nitric acid. Collect these reagents and carefully add them to your volumetric flasks. When your solutions are prepared, measure the absorbance of each solution twice and tabulate your absorbance data in an organized manner. An example data table is shown in Table 2.

Reactants	Experiment number					
	1	2	3	4	5	6
Volume of $Fe[(H_2O)]3NO_3$	5.0 mL	5.0 mL	5.0 mL	5.0 mL	5.0 mL	5.0 mL
Volume of KSCN	0.0 mL	1.0 mL	2.0 mL	3.0 mL	4.0 mL	5.0 mL
Volume of 0.1 M HNO_3	20.0 mL	19.0 mL	18.0 mL	17.0 mL	16.0 mL	15.0 mL

Table 1.

Stock conc. of $Fe[(H_2O)_6]3NO_3$: __________ Stock conc. of KSCN: ____________

Trial #	Beer's Law Data		
	Conc. of $[FeNCS]^{2+}$	Abs. at _______ nm	ε ($M^{-1}cm^{-1}$)
1			
2			
3			
4			
5			
6			

Table 2.

Part II: Determination of the Equilibrium Constant

Now repeat the above procedure but use the amounts of reactants noted in **Table 3**. The concentration of the reactants and products can be determined from absorbance data using the Beer's Law plot generated in Part I. Record your data in a table (see example Table 4).

Reactants	Experiment number					
	1	2	3	4	5	6
Volume of $Fe[(H_2O)]3NO_3$	5.0 mL	5.0 mL	5.0 mL	5.0 mL	5.0 mL	5.0 mL
Volume of NaSCN	0.0 mL	1.0 mL	2.0 mL	3.0 mL	4.0 mL	5.0 mL
Volume of 0.1 M HNO_3	5.0 mL	4.0 mL	3.0 mL	2.0 mL	1.0 mL	0.0 mL

Table 3.

Stock concentration of $Fe[(H_2O)_6]3NO_3$: ____________ Stock concentration of KSCN: ______________

Trial #	Final Concentrations and Calculated Equilibrium Constant				
	Abs.	$[SCN^-]$	$[Fe^{3+}]$	$[FeNCS]^{2+}$	K
1					
2					
3					
4					
5					
6					

Table 4.

Part III: Temperature Dependence of K, the equilibrium constant

In this experiment we want to see if the equilibrium constant K is temperature dependent. You will use two water baths, one warmer than room temperature and one cooler.

Select a group of experimental conditions from Part II of this experiment. Try to pick conditions that give an Absorbance near 1.0. Pour enough of the reaction mixture into three separate vials and then place these in the water baths until the temperature has equilibrated. Measure the absorbance as done before. Do not lollygag between the time your remove your sample from the ice bath until you make your measurement. Record your data in an organized table as suggested below.

	Abs.	$[SCN^-]$	$[FeNCS]^{2+}$	K
T (cold):______				
Room temp:_______				
T(hot):________				

Table 5.

Starting concentrations for Part III: _____________________ _____________________

CLEAN UP

Do not leave without fully cleaning your workstation and asking Sina about a community cleaning job.

Continue to the Post-lab in class if time allows, or complete it outside of class.

__Postlab__

It should be done in your lab notebook and turned in at the beginning of class next Monday Jan. 25th at 10:00 AM

1. Attach a print-out of a clear and organized Beer's Law plot including the equation for the line of best fit. Note: the y-axis is absorbance and x-axis is concentration. What is the molar absorptivity, ε, of the $[FeNCS]^{2+}$ complex at the wavelength used?

2. Calculate the final concentrations and equilibrium constants and complete your data tables. Summarize your results in paragraph format here (be sure to reference your data tables).

3. Suppose we used the sodium salt of the thiocyanate instead of the potassium salt. Explain how you would prepare 2 liters of a solution of 0.002 M NaSCN. Considering the mass of NaSCN necessary, use the website Sigma-Aldrich to determine the approximate cost of preparing your 2 L solution.

4. Calculate the pH of a 0.1 M nitric acid. Explain how doing this experiment in 0.1 M nitric acid prevents the iron complex from giving up a proton. Hint: the pK_a of the reaction shown in Figure 2 is 3.1.

5. In the Prelab assignment you made a hypothesis regarding Part 3 of this lab. Did the experimental results support or refute your hypothesis? How confident are you in your conclusions? Discuss the reliability of our experimental methods. Suggest ways to improve the accuracy of our measurements (or suggest different, more accurate measurements that would achieve the same goals).