

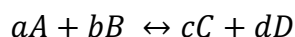
Objective

To determine the equilibrium constant (K) for the reaction of the iron (III) ion with thiocyanate (SCN^-) to form the thiocyanatoiron(III) complex ion (FeSCN^{2+}). This measurement is done by monitoring the concentration of the thiocyanatoiron(III) complex ion through its absorption of light.

Background

To get the most benefit from this lab, you should read sections 14.2-14.3 of Tro (3rd ed). You should also bring the portion of the aspirin procedure that deals with setting up and using the Spec-20.

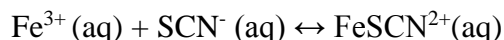
Not all chemical reactions go to completion. Instead, they reach a point where the rates of the forward and reverse reactions are equal, known as a dynamic equilibrium. When a reaction is at equilibrium, an equilibrium constant (K) can be calculated using the concentrations of the reactants and the products. The value of K is constant for the reaction regardless of the initial concentrations of the components, but is temperature dependent. For the generic reaction:



the expression for the equilibrium constant, K, is:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

In this lab, you will determine the equilibrium constant for the reaction of iron (III) ion with thiocyanate (SCN^-) to form the thiocyanatoiron(III) complex ion (FeSCN^{2+}).



The expression for the equilibrium constant for this reaction is:

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

In order to determine the value of K for this reaction, we need to determine the concentrations of each of the three ions in the solution. Because the thiocyanatoiron(III) complex (FeSCN^{2+}) is red, we will be able to use absorption spectroscopy to monitor its concentration using the Beer-Lambert law where the absorption of light is related to the product of the molar absorptivity (ϵ), the path length (b) and the molar concentration (c) of the absorbing species:

$$A = \epsilon bc$$

In order to calculate the absorbance (A) of light at each wavelength, the intensity of the light that reaches the detector when no sample is present (I_0) must be compared to the intensity of the light transmitted when the sample is present (I_t). The ratio of these intensities corresponds to the **transmittance (T)** at that wavelength. The **percent transmittance (%T)** is commonly reported by instrumentation. A is related to the light intensities and the %T through the expression:

$$A = \log \left(\frac{I_0}{I_t} \right) = 2.00 - \log(\%T)$$

At 447 nm, only the complex ion should absorb, making the Beer-Lambert law

$$A = \epsilon b [FeSCN^{2+}]$$

We will first rearrange this expression to solve for $[FeSCN^{2+}]$. Because the system will be at equilibrium when we measure the absorbance, the concentration we determine will be the equilibrium concentration and can be substituted into the K expression for the chemical system.

$$[FeSCN^{2+}] = \frac{A}{\epsilon b}$$

$$K = \frac{\frac{A}{\epsilon b}}{[Fe^{3+}][SCN^{-}]}$$

Now, we need to find a way to relate the equilibrium concentrations of the reactants (Fe^{3+} and SCN^{-}) to values that we know. We are able to control and calculate the initial concentrations (before any complex is formed) of Fe^{3+} and SCN^{-} that are added to the system (designated as $[Fe^{3+}]_0$ and $[SCN^{-}]_0$). After equilibrium is achieved, the concentrations of the reactants will have decreased from their original values but will still be equal to the sum of the reactant and product. These expressions are shown below:

$$[Fe^{3+}]_0 = [Fe^{3+}] + [FeSCN^{2+}]$$

$$[SCN^{-}]_0 = [SCN^{-}] + [FeSCN^{2+}]$$

We will substitute $\frac{A}{\epsilon b}$ for $[FeSCN^{2+}]$ and rearrange these expressions to solve for the equilibrium concentrations of Fe^{3+} and SCN^{-} . Then, we are able to rewrite the expression for K using constants and values that you can calculate or measure.

$$[Fe^{3+}] = [Fe^{3+}]_0 - \frac{A}{\epsilon b}, \quad [SCN^{-}] = [SCN^{-}]_0 - \frac{A}{\epsilon b}$$

$$K = \frac{\frac{A}{\epsilon b}}{\left([Fe^{3+}]_0 - \frac{A}{\epsilon b}\right)\left([SCN^-]_0 - \frac{A}{\epsilon b}\right)}$$

Although the math is complex, it was shown by H.A. Frank and R. L. Oswalt (*J. Am. Chem. Soc.* **1947**, 69, 1321) that the following equation can be derived from the expression of K:

$$\underbrace{\frac{A}{[Fe^{3+}]_0 \times [SCN^-]_0}}_y = -K \times \underbrace{\left[\frac{A([Fe^{3+}]_0 + [SCN^-]_0)}{[Fe^{3+}]_0 \times [SCN^-]_0} \right]}_x + \underbrace{\epsilon b K}_b$$

While this equation looks extremely complex, it is really just the equation of a line! When you plot this, the slope of the line is equal to $-K$.

Procedure

For this procedure, you will need the following glassware and supplies:

- Beaker or Erlenmeyer holding about 20 mL of KSCN solution
 - Beaker or Erlenmeyer containing about 40 mL of 2 M HNO₃
 - Beaker or Erlenmeyer containing about 20 mL of 0.5 M HNO₃
 - Beaker or Erlenmeyer containing about 20 mL of Fe(NO₃)₃/HNO₃ solution
 - 1 cuvet and test tube rack
 - 250 mL beaker
 - 100 mL volumetric flask
 - 1 mL volumetric pipet
 - 20 mL volumetric pipet
 - 10 mL volumetric pipet
 - 25 mL volumetric pipet
 - glass stirring rod
1. Turn on the Spec-20 to allow it to warm before you need to use it for measurement. You will need to set the wavelength to 447 nm and check that the filter lever is in the appropriate position.
 2. Clean the 100-mL volumetric flask, and the volumetric pipets by rinsing them three times with deionized water. Rinse the 100-mL volumetric flask with a small aliquot of 0.5 M HNO₃.

3. Rinse the 10 mL pipet with a small portion of KSCN and discard. Then, add 10 mL of KSCN to the 100 mL volumetric flask.
4. After also rinsing the 25 mL pipette with a small portion of 2 M HNO_3 , add 25 mL of 2 M HNO_3 to the 100 mL volumetric flask.
5. Add enough deionized water to fill to the neck of the volumetric flask and mix the solution. Carefully add deionized water to the graduation mark using a plastic Pasteur pipet. After mixing the solution, transfer to a clean, dry 250 mL beaker.
6. Rinse the 1 mL pipette twice with portions of the $\text{Fe}(\text{NO}_3)_3/\text{HNO}_3$ solution. Then, add 1 mL of the $\text{Fe}(\text{NO}_3)_3/\text{HNO}_3$ solution to the KSCN/ HNO_3 solution in the 250 mL beaker.
7. Mix the solution in the beaker thoroughly with a clean, dry stirring rod. Leave the stirring rod in the beaker.
8. Using a plastic Pasteur pipet, add 0.5 M HNO_3 to the cuvette to use as the blank for the Spec-20. Follow the directions for setting up the Spec-20 that were provided as part of the Aspirin Determination Lab. Discard the blank.
9. Using a clean plastic Pasteur pipet, transfer a portion of the equilibrium mixture to the cuvet and record the absorbance of the solution at 447 nm. **DO NOT DISCARD THIS SOLUTION!** You need to return this solution to the equilibrium mixture before continuing. Make sure that you get as much of the solution back into the mixture as possible. Do not rinse the cuvet.
10. Using a 1 mL volumetric pipet, transfer 1 mL of the $\text{Fe}(\text{NO}_3)_3/\text{HNO}_3$ solution to the reaction mixture. Stir well.
11. Using the Pasteur pipet from Step 9, transfer a portion of the new equilibrium mixture to the cuvet and record the absorbance of the solution at 447 nm. Return this solution to the equilibrium mixture when the absorbance measurement is complete.
12. Repeat Steps 10 and 11 eight more times until you have measured absorbances for a total of 10 reaction mixtures.
13. Dispose of all solutions according to your laboratory instructor's direction. Clean and return all glassware. Discard all Pasteur pipets.

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Data Sheet

Record from Original Bottles:

_____ molarity of stock KSCN (M)

_____ molarity of $\text{Fe}(\text{NO}_3)_3$ solution (M)

Measure from lab:

_____ volume (mL) of stock KSCN solution used

Calculate:

_____ molarity of diluted KSCN solution (M)

_____ wavelength (nm)

447 nm

Reaction Mixture	<u>Total</u> volume of $\text{Fe}(\text{NO}_3)_3$ solution added to system*	Total volume of system	Absorbance Measurement
1	1.00 mL	101 mL	
2	2.00 mL	102 mL	
3	3.00 mL	103 mL	
4			
5			
6			
7			
8			
9			
10			

* Note: You will only add 1 mL of the $\text{Fe}(\text{NO}_3)_3$ at a time. This column is a sum of those additions.

Calculations

Because the following calculations are repeated for each of the ten equilibrium mixtures, it is recommended that you use Excel or a similar program to perform these calculations. If you use a spreadsheet, you may be asked to print and fill out the Results table on the following page.

1. Calculate the original molarity of the diluted KSCN solution from Step 4. This is the value you should record on your Data Sheet.
2. Calculate the $[\text{SCN}^-]_0$ for each measurement.
Hint: Use $M_1V_1=M_2V_2$ for this calculation. The values of M_1 and V_1 will be the same for all 10 of the calculations. Use the total volume of the equilibrium solution as V_2 and calculate and record M_2 . Note that the value of V_2 changes by 1 mL with each successive equilibrium mixture.
3. Record $[\text{Fe}^{3+}]_0$ for each measurement.
Again use $M_1V_1=M_2V_2$ for this calculation. M_1 is the concentration of the $\text{Fe}(\text{NO}_3)_3$ found on the stock bottle. V_1 is the volume of that stock added to the reaction mixture (1-10 mL), and V_2 is the total volume of the reaction mixture.
4. Next begin a series of simple algebraic steps to compute the values that are need for x and y in the equation given in the Background section:

$$\underbrace{\frac{A}{[\text{Fe}^{3+}]_0 \times [\text{SCN}^-]_0}}_y = \underbrace{-K}_{m} \times \underbrace{\left[\frac{A([\text{Fe}^{3+}]_0 + [\text{SCN}^-]_0)}{[\text{Fe}^{3+}]_0 \times [\text{SCN}^-]_0} \right]}_x + \underbrace{\epsilon b K}_b$$

5. Plot, and using a line of best fit, determine the value of K (remember that slope is equal to $-K$). Also note that K is unit-less.

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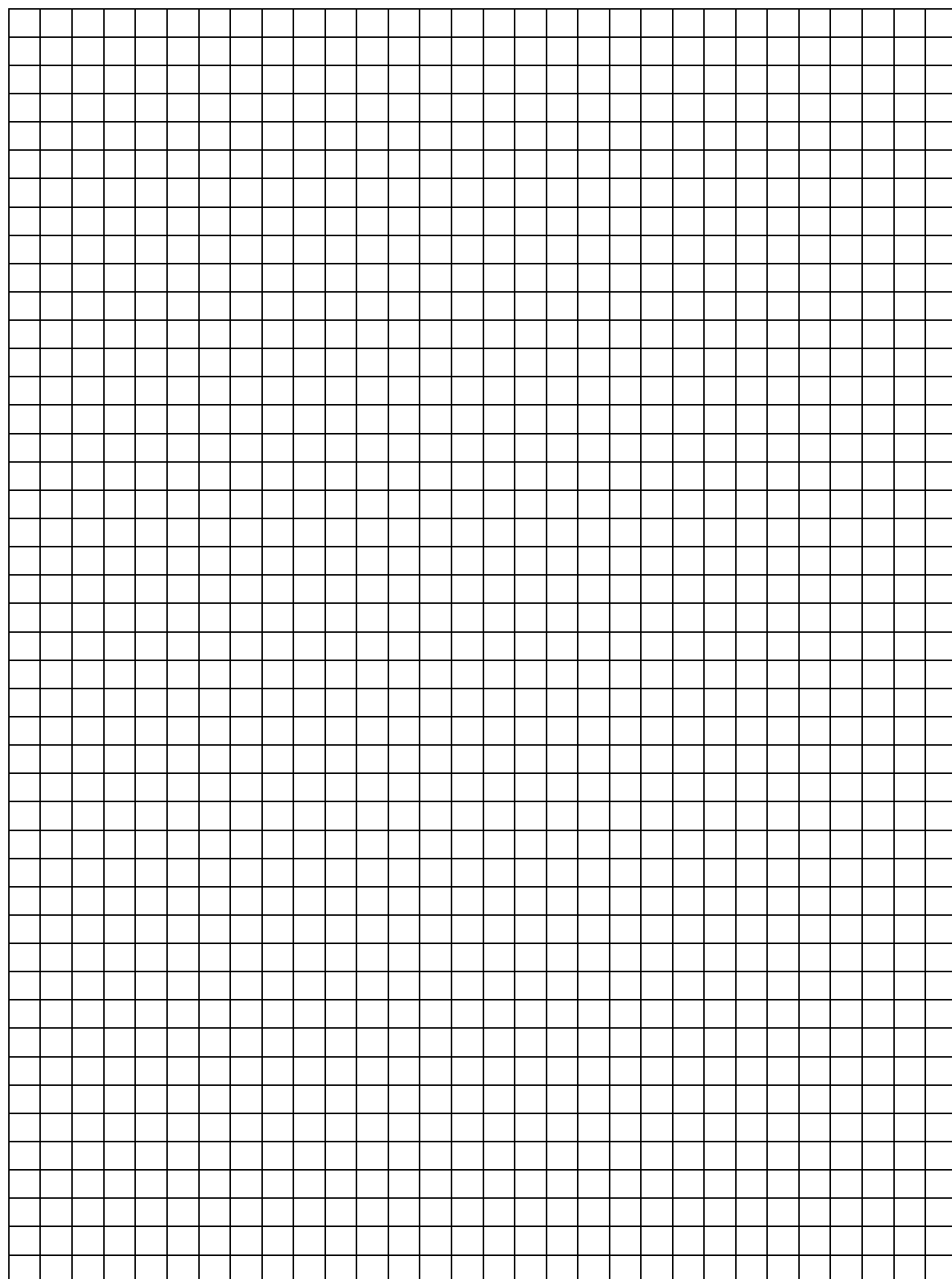
Results

y

x

Reaction Mixture	$[Fe^{3+}]_0$	$[SCN^-]_0$	$\frac{A}{[Fe^{3+}]_0 \times [SCN^-]_0}$	$\frac{A([Fe^{3+}]_0 + [SCN^-]_0)}{[Fe^{3+}]_0 \times [SCN^-]_0}$
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				

Equation of Best Fit Line	
R ² Value	
Slope of Line	
Value of K, the Equilibrium Constant	



NAME _____

Post Lab Assignment

1. Record the value of the equilibrium constant that you determined for this chemical system, and write the equilibrium constant expression for this system.
2. Frank and Oswalt report a molar absorptivity (ϵ) for FeSCN^{2+} of $4700\text{L}/(\text{mol}\cdot\text{cm})$. Remember that your pathlength (b) is 1 cm for the Spec-20. Using the absorbance that you measured after adding 1.00 mL of $\text{Fe}(\text{NO}_3)_3$ to the reaction mixture, what is the equilibrium concentration for FeSCN^{2+} in that first solution?

3. Using your value for K and the $[\text{FeSCN}^{2+}]$ calculated above, and the initial concentrations of Fe^{3+} and SCN^- from your results sheet, calculate the equilibrium concentrations for Fe^{3+} , SCN^- for the system in the first measurement where only 1.00 mL of $\text{Fe}(\text{NO}_3)_3$ is added. *Hint: Use the following equations:*

$$[\text{Fe}^{3+}]_0 = [\text{Fe}^{3+}] + [\text{FeSCN}^{2+}]$$

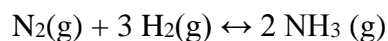
$$[\text{SCN}^-]_0 = [\text{SCN}^-] + [\text{FeSCN}^{2+}]$$

4. Are the concentrations you calculated reasonable? Explain based on your value of K .

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Pre-Lab Assignment

1. In this procedure, why is it critical that after each absorbance measurement you return the solution from the cuvet back into the reaction mixture?
2. Why are you instructed to use 0.5 M HNO₃ as the blank for your absorbance measurements rather than distilled water?
3. Write the equilibrium constant expression (K) for the following reaction:



4. For the equilibrium in question #3, if the value of K at 25°C is 3.7×10^8 , and the equilibrium concentrations for N₂ and H₂ are $1.05 \times 10^{-4}\text{M}$ and $5.42 \times 10^{-5}\text{M}$, respectively, use the expression above to calculate the equilibrium concentration of NH₃.