

# Determination of an Equilibrium Constant

## PURPOSE

To determine the equilibrium constant for the reaction:



## GOALS

- 1 To gain more practice using a pipet properly.
- 2 To gain more practice diluting stock solutions.
- 3 To gain more practice using a spectrophotometer.
- 4 To gain practice plotting a calibration curve and use it to determine the concentration of an unknown solution.

## INTRODUCTION

A typical chemical equation has the following form:



This form of the equation assumes that the reaction proceeds completely to products. In practice, many reactions do not proceed to completion. If we measure the concentration of a reactant, it eventually reaches a value that does not change further over time. If we measure the concentration of a product, it reaches a constant value short of that predicted by the theoretical yield calculation. In these cases, we say that the reaction has reached equilibrium<sup>1</sup>. We write the chemical reaction using equilibrium arrows instead of a single arrow:



At equilibrium, the rates of the forward and reverse reactions are equal and, unless equilibrium is disturbed (stressed), no changes in reactant or product concentrations will be measured. The equilibrium arrows, one of which points in each direction, reinforce this idea.

At equilibrium, the molar concentrations of products and reactants will be fixed in a given ratio. This ratio is the equilibrium constant,  $K_{eq}$ , which is determined by substituting molar concentrations (indicated by the square brackets) into the equilibrium constant equation. The general form of this equation is:

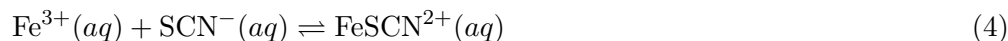
$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \tag{3}$$

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<sup>1</sup><http://en.wikipedia.org/wiki/Equilibrium>

Reactants mixed in arbitrary concentrations will react until the ratio of the concentrations reaches the value of the equilibrium constant according to equation 3. The value of  $K_{eq}$  varies with temperature; therefore, the temperature at which the equilibrium constant was determined must be referenced.

In this laboratory experiment, a combination of solution chemistry, stoichiometry, and spectrophotometric analysis will be used to determine the equilibrium constant for a reaction between the iron (III) ion ( $\text{Fe}^{3+}$ ) and the thiocyanate ion ( $\text{SCN}^-$ ). In acidic solution, these ions form a blood-red complex ion as shown in equation 4:



The equilibrium constant for equation 4 can be expressed using the concentrations of the three components:

$$K = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} \quad (5)$$

In order to calculate the equilibrium constant, one must simultaneously determine the concentrations of all three of the components. In this experiment, you will measure the concentration of  $\text{FeSCN}^{2+}$  at equilibrium by measuring its absorbance at 470 nm. Since  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  do not absorb light at this wavelength, they do not interfere with the measurements. If you know the initial (before equilibrium) concentrations of  $\text{Fe}^{3+}$  and  $\text{SCN}^-$ , you can use a reaction table to calculate the equilibrium concentrations of these two ions at equilibrium.

For example, you might initially mix equal volumes of 2.0 M  $\text{Fe}^{3+}$  and 2.0 M  $\text{SCN}^-$ . The term “initial concentration” can be confusing. Even though the reaction appears to take place instantaneously upon mixing the reactants, the “initial concentrations” in the reaction table are those after dilution has been taken into consideration but before any reaction occurs. Thus, the initial line in the reaction table for mixing equal volumes of 2.0 M  $\text{Fe}^{3+}$  and 2.0 M  $\text{SCN}^-$  should have entries of 1.0 M under  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  due to dilution. The initial concentration of  $\text{FeSCN}^{2+}$  is 0.0 M. In our example, you might measure an equilibrium (final) concentration of 0.6 M  $\text{FeSCN}^{2+}$ . With the final concentration of the product, you can determine the change in product concentration and, therefore, the changes in the reactant concentrations. The reaction table is shown below:

	$\text{Fe}^{3+}$	+	$\text{SCN}^-$	=	$\text{FeSCN}^{2+}$
initial	1.0 M		1.0 M		0.0 M
$\Delta$	-0.6 M		-0.6 M		+0.6 M
equilibrium (final)	0.4 M		0.4 M		0.6 M

In this experiment, 0.2 M  $\text{HNO}_3$  serves as the solvent. The acid adds a large (compared to the reactants) amount of  $\text{H}^+$ . This prevents side reactions such as the formation of  $\text{FeOH}^{2+}$ , a brownish species that can affect the results. The acid concentration is high enough that it is not affected by the reaction and remains constant at 0.2 M.

You will prepare six standard solutions of  $\text{FeSCN}^{2+}$  to calibrate a spectrophotometer. A fair

question is "How do I know the concentration of  $\text{FeSCN}^{2+}$  in my standard solutions if it is in equilibrium with  $\text{Fe}^{3+}$  and  $\text{SCN}^-$ ?" In the standard solutions, the concentration of  $\text{Fe}^{3+}$  is much higher than that of  $\text{SCN}^-$ . This forces the equilibrium as far to the right (toward  $\text{FeSCN}^{2+}$ ) as possible. Therefore, the concentration of  $\text{FeSCN}^{2+}$  in a standard solution will be very nearly equal to the initial concentration of  $\text{SCN}^-$  used in preparing it. The absorbance measurement at 470 nm will correlate to the concentration of complex ion, and an accurate calibration curve (Beer's Law plot) can be obtained. Recall that the calibration curve gives you a relationship between the concentration of a species in solution and its absorbance at a given wavelength: ( $A = \epsilon l c$ ). Using the linear regression of the calibration curve in Part A, you will determine the concentration of  $\text{FeSCN}^{2+}$  ion in each of five equilibrium mixtures in Part B. An equilibrium constant can then be calculated for each mixture; the average of all of these values should be reported as the equilibrium constant value for the formation of the  $\text{FeSCN}^{2+}$  ion.

In Part A of this experiment, you will prepare  $\text{FeSCN}^{2+}$  solutions of known concentrations, measure their absorbance at 470 nm, and produce a calibration curve. In Part B, you will make equilibrium mixtures of  $\text{Fe}^{3+}$ ,  $\text{SCN}^-$ , and  $\text{FeSCN}^{2+}$ . You will determine the concentration of  $\text{FeSCN}^{2+}$  from its absorbance at 470 nm and your calibration curve from Part A. Then, using reaction tables, you will calculate the equilibrium concentrations of  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  and use those values to determine the equilibrium constant for the formation of  $\text{FeSCN}^{2+}$ . You will calculate the equilibrium constant for each mixture you prepare and then use each value to find the average equilibrium constant for the formation of  $\text{FeSCN}^{2+}$ .

## EQUIPMENT

- 1 MicroLab Spectrophotometer
- 1 MicroLab Spectrophotometer Instruction
- 6 vials
- 3 Serological pipets
- 1 pipet bulb
- 3 30 mL beakers for reagents
- 6 13×100 mm test tubes for mixtures
- 6 stoppers
- 1 test tube rack
- 1 250 mL beaker for waste
- 1 deionized water squirt bottle

## REAGENTS

~10 mL 0.100 M  $\text{Fe}(\text{NO}_3)_3$  in 0.2 M  $\text{HNO}_3$

~10 mL  $6.00 \times 10^{-4}$  M  $\text{NaSCN}$  in 0.2 M  $\text{HNO}_3$

~15 mL 0.002 M  $\text{Fe}(\text{NO}_3)_3$  in 0.2 M  $\text{HNO}_3$

~15 mL 0.002 M NaSCN in 0.2 M HNO<sub>3</sub>

## SAFETY

Nitric acid is listed as a corrosive. Corrosives can attack the skin and cause permanent damage to the eyes. Nitric acid and iron(III) nitrate are listed as oxidants. Sodium thiocyanate is listed as toxic and an irritant. With the exception of nitric acid, the concentrations of all these materials are quite low, however. If you spill any of these chemicals on skin or clothing, immediately rinse the affected area with water for at least 15 minutes and have your lab partner notify the teaching assistant.

Students will have access to gloves due to the use of acidic sodium thiocyanate solutions during the lab period.

## WASTE DISPOSAL

All of the solutions prepared in this experiment, as well as excess NaSCN solution, should be discarded in the waste container. Collect your waste in a labeled waste beaker while you are carrying out the experiment, and then dispose of the waste in your section's waste container at the end of the lab period. Always remember not to overfill the waste bottle. If your waste bottle is full, please alert your teaching assistant.

## PRIOR TO CLASS

Please read the following section of Lab Safety and Practices:

Good Lab Practices<sup>2</sup>

Plotting a Calibration Curve<sup>3</sup>

Please read the following section of Lab Equipment:

Volumetric Glassware<sup>4</sup>

Please review the following videos:

Safety<sup>5</sup>

Pipeting Techniques<sup>6</sup>

Please complete WebAssign prelab assignment. Check your WebAssign Account for due dates. Students who do not complete the WebAssign prelab are required to bring and hand in the prelab worksheet.

## LAB PROCEDURE

Please print the worksheet for this lab. You will need this sheet to record your data.

### Part A: Preparation of Standard Solutions and Beer's Law Plot

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<sup>2</sup>../practices/manual.html

<sup>3</sup>../graphs/manual.html

<sup>4</sup>../equipment/manual.html#volumetric glassware

<sup>5</sup>[https://www.youtube.com/watch?v=S\\_mm-PF\\_Iq8](https://www.youtube.com/watch?v=S_mm-PF_Iq8)

<sup>6</sup><https://www.youtube.com/watch?v=03Yxg0lb0dA>

- 1 A spectrophotometer will be set up in your work area. Make sure it is turned on and allow it to warm up.
- 2 While the spectrophotometer is warming up, obtain three serological pipets, and label a beaker for waste.
- 3 Obtain about 10 mL of 0.100 M  $\text{Fe}(\text{NO}_3)_3$  in 0.2 M  $\text{HNO}_3$  in a small, clean, dry beaker. Obtain about 10 mL of  $6.00 \times 10^{-4}$  M  $\text{NaSCN}$  in 0.2 M  $\text{HNO}_3$  in another beaker. Label the solutions so you do not mix them up.
- 4 Condition one pipet for each of the solutions you obtained in step 3 and one for deionized water. This procedure is shown in the “Pipeting Techniques” linked to in the **PRIOR TO CLASS** section above and is also described in the “Volumetric Glassware” section of the Introductory Material of this lab manual, which is also linked to in **PRIOR TO CLASS** above.
- 5 Using the conditioned pipets, add the amounts of the  $\text{Fe}^{3+}$  solution,  $\text{SCN}^-$  solution and water listed in Data Table A for the Blank and Solutions 1A - 4A to five labeled test tubes. Stopper each test tube and invert a few times to mix each solution.
- 6 Once the spectrophotometer is warmed up, take a spectrum with your Blank solution. To condition your vial, carefully pour a small amount of the Blank solution into a vial and pour it out to waste. Refer to the MicroLab Spectrophotometer Instructions provided in lab.
- 7 Condition a vial using Solution 1A, refill the vial, measure its **absorbance at  $\sim 470$  nm** and record this value in Data Table A. When finished, retain this sample in your vial until you have completed your calibration plot. Students often choose to label a sheet of paper with positions 1A, 2A, etc., placing each vial on the appropriate position.
- 8 Repeat step 7 for each of the remaining solutions from Data Table A.
- 9 The MicroLab software will plot the absorbance of the  $\text{FeSCN}^{2+}$  solutions as a function of their concentrations. The trendline and  $R^2$  value are displayed. If your plot is linear with an  $R^2$  value of 0.9 or greater, continue the experiment. If your  $R^2$  value is low, consult with your TA. Record the trendline and  $R^2$  value in Data Table A. **Do not close the MicroLab file**, as this calibration will be used to determine concentrations in Part B.
- 10 Safely dispose of the calibration solutions in your labeled waste beaker.
- 11 Discard any remaining 0.100 M  $\text{Fe}(\text{NO}_3)_3$  in 0.2 M  $\text{HNO}_3$  and  $6.00 \times 10^{-4}$  M  $\text{NaSCN}$  in 0.2 M  $\text{HNO}_3$  in the labeled waste container. Rinse and dry your beakers for use in Part B.

**WA**

**Table A:** Calibration Curve of  $\text{FeSCN}^{2+}$  Solutions

**WA**

**Question 1:** What is the initial concentration of  $\text{SCN}^-$  in Solution 1A? Show your work; remember to account for dilution. Pay attention to significant figures.

**WA**

**Question 2:** Given your result from Question 1, what is the concentration of  $\text{FeSCN}^{2+}$  in Solution 1A? Enter this concentration in your data table.



**Question 3:** How does the intensity of the color of the solutions and the absorbance vary with the concentration of the  $\text{FeSCN}^{2+}$  solution?

### Part B: Preparation of the Equilibrium Mixtures and Absorbance Measurements

- 1 Obtain about 15 mL of 0.002 M  $\text{Fe}(\text{NO}_3)_3$  in 0.2 M  $\text{HNO}_3$  in a small, clean, dry beaker. Obtain about 15 mL of 0.002 M  $\text{NaSCN}$  in 0.2 M  $\text{HNO}_3$  in another beaker. Label the solutions so you do not mix them up.
- 2 Re-condition your pipets with the new solutions of  $\text{Fe}^{3+}$  and  $\text{SCN}^-$ .
- 3 Using the conditioned pipets, add the amounts of the  $\text{Fe}^{3+}$  solution,  $\text{SCN}^-$  solution and water required for Solutions 1B - 5B listed in Data Table B to 5 labeled test tubes. Stopper each test tube and invert a few times to mix the solutions.
- 4 Measure the absorbance of each solution as an unknown sample, not part of the calibration plot, and record them in Data Table B.



**Table B:** Measuring  $[\text{FeSCN}^{2+}]$  in Equilibrium Mixtures



**Question 4:** Calculate the initial concentration of  $\text{Fe}^{3+}$  in Solution 1B. Show your work; remember to account for dilution. Enter the concentration in your data table.



**Question 5:** Calculate the initial concentration of  $\text{SCN}^-$  in Solution 1B. Show your work; remember to account for dilution. Enter the concentration in your data table.



**Question 6:** Using your calibration curve from Part A and your absorbance data from Part B, what is the equilibrium concentration of  $\text{FeSCN}^{2+}$  in Solution 1B? Show your work.



**Question 7:** Construct a reaction table for Solution 1B.

	$\text{Fe}^{3+}(\text{aq})$	+	$\text{SCN}^-(\text{aq})$	$\rightarrow$	$\text{FeSCN}^{2+}(\text{aq})$
<b>initial</b>					
<b>change(<math>\Delta</math>)</b>					
<b>equilibrium</b>					



**Question 8:** From the equilibrium concentrations in the reaction table for Solution 1B, calculate the equilibrium constant for the reaction.

You will complete the calculations for the remaining solutions as part of the WebAssign postlab assignment.

- 5 When you are finished taking measurements, collect all your waste and place it in the waste bottle in the lab, making sure not to overfill it. Rinse and dry all your glassware with water and return it to the set-up area where you found it. Close the MicroLab software.

- 6 Remember to show your TA your calibration curve, reaction table, and equilibrium constant calculation. Your TA will manually grade the results and enter your score into WebAssign.
- 7 Before leaving, enter your results in the InLab assignment. If all results are scored as correct, log out. If not all results are correct, try to find the error or consult with your teaching assistant. When all results are correct, note them and log out of WebAssign. The InLab assignment must be completed by the end of the lab period. If additional time is required, please consult with your teaching assistant.