The Determination of an Equilibrium Constant

Chemical reactions occur to reach a state of equilibrium. The equilibrium state can be characterized by quantitatively defining its equilibrium constant, K_{eq}. In this experiment, you will determine the value of Keq for the reaction between iron (III) ions and thiocyanate ions, SCN–.

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightarrow FeSCN^{2+}(aq)$$

The equilibrium constant, K_{eq}, is defined by the equation shown below.

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

To find the value of K_{eq}, which depends only upon temperature, it is necessary to determine the molar concentration of each of the three species in solution at equilibrium. You will determine the concentration by measuring light that passes through a sample of the equilibrium mixtures. The amount of light absorbed by a colored solution is proportional to its concentration. The red $FeSCN^{2+}$ solution absorbs blue light, thus the Colorimeter users will be instructed to use the 470 nm (blue) LED. Spectrometer users will determine an appropriate wavelength based on the absorbance spectrum of the solution.

In order to successfully evaluate this equilibrium system, it is necessary to conduct three separate tests. First, you will prepare a series of standard solutions of $FeSCN^{2+}$ from solutions of varying concentrations of SCN^{-} and constant concentrations of H^{+} and Fe^{3+} that are in stoichiometric excess. The excess of H^{+} ions will ensure that Fe^{3+} engages in no side reactions (to form $FeOH^{2+}$, for example). The excess of Fe^{3+} ions will make the SCN^{-} ions the limiting reagent, thus all of the SCN^{-} used will form $FeSCN^{2+}$ ions. The $FeSCN^{2+}$ complex forms slowly, taking at least one minute for the color to develop. It is best to take absorbance readings after a specific amount of time has elapsed, between two and four minutes after preparing the equilibrium mixture. Do not wait much longer than four minutes to take readings, however, because the mixture is light sensitive and the $FeSCN^{2+}$ ions will slowly decompose.

In Part II of the experiment, you will analyze a solution of unknown [SCN^{-}] by using the same procedure that you followed in Part I. In this manner, you will determine the molar concentration of the SCN^{-} solution using your calibration curve.

Third, you will prepare a new series of solutions that have varied concentrations of the Fe^{3+} ions and the SCN^{-} ions, with a constant concentration of H^{+} ions. You will use the results of this test to accurately evaluate the equilibrium concentrations of each species.

OBJECTIVES

In this experiment, you will

- Prepare and test standard solutions of $FeSCN^{2+}$ in equilibrium.
- Test solutions of SCN^{-} of unknown molar concentration.
- Determine the molar concentrations of the ions present in an equilibrium system.
- Determine the value of the equilibrium constant, K_{eq}, for the reaction.

MATERIALS

Check out from Stockroom
Vernier LabQuest
LabQuest App
Vernier Colorimeter or Spectrometer
plastic cuvette
pipet pump or bulb
50 mL volumetric flask

In the classroom
0.200 M iron (III) nitrate, $Fe(NO_3)_3$, solution in 1.0 M HNO_3
0.0020 M iron (III) nitrate, $Fe(NO_3)_3$, solution in 1.0 M HNO_3
potassium thiocyanate, KSCN solution of unknown concentration
0.0020 M thiocyanate, SCN^-
plastic Beral pipets
tissue
six 20 × 150 mm test tubes & test tube rack
eight 100 mL beakers

PROCEDURE

Part I: Prepare and Test Standard Solutions

1. Obtain and wear goggles.

2. Obtain small volumes, approximately 35 mL of 0.200 M $Fe(NO_3)_3$, and 25 mL of 0.0020 M SCN^-, in 2 separate small Erlenmeyer flasks. **CAUTION:** *$Fe(NO_3)_3$ solutions in this experiment are prepared in 1.0 M HNO_3 and should be handled with care.* Place fresh DI (distilled) water in a wash bottle. Label five beakers: 1–5. Prepare the respective five solutions listed in the chart below (The fifth beaker is a blank.), all to 50 mL. This is done by using a clean 10.0 mL pipet with bulb to transfer the respective $Fe(NO_3)_3$ solution to a 50-mL volumetric flask and a different clean 10.0 mL pipet to transfer the corresponding SCN- solution to the same 50-mL volumetric flask. Now add enough DI water to make exactly 50 mL of solution. Read the bottom of the meniscus to the fill line. Mix each solution thoroughly. Repeat this process for each trial, remembering to clean the volumetric flask thoroughly. Measure and record the temperature of one of the above solutions to use as the temperature for the equilibrium constant, K_{eq}.

Beaker number	0.200 M $Fe(NO_3)_3$ (mL)	0.0020 M SCN^- (mL)
1	5.0	2.0
2	5.0	3.0
3	5.0	4.0
4	5.0	5.0
blank	5.0	0.0

Note: The fifth beaker is prepared to be used as a blank for your Colorimeter calibration. It will have a slightly yellow color due to the presence of $Fe(NO_3)_3$. By calibrating with this solution as your blank, instead of distilled water, you will account for this slight yellow color.

3. Prepare a *blank* by filling a cuvette 3/4 full of the solution in the fifth beaker. To correctly use cuvettes, remember:
   - Wipe the outside of each cuvette with a lint-free tissue.
   - Handle cuvettes only by the top edge of the ribbed sides.
   - Dislodge any bubbles by gently tapping the cuvette on a hard surface.
   - Always position the cuvette so the light passes through the clear sides.

4. Connect the Colorimeter to LabQuest and choose **New** from the **File** menu on top.

5. Calibrate the Colorimeter.
   a. Place the ***blank*** in the cuvette slot of the Colorimeter and close the lid.
   b. Press the < or > buttons on the Colorimeter to set the wavelength to 470 nm. Press the CAL button on the Colorimeter. When the LED stops flashing, the calibration is complete.

6. Set up the data-collection mode.
   a. On the Meter screen to the top right, tap **Mode**. Change the mode to **Events with Entry**.
   b. Enter the **Name** (Concentration) and **Units** (mol/L). Select **OK**.
   c. NOTE: Do not stop until data entry is complete.

7. Collect absorbance-concentration data for the four standard solutions in Beakers 1-4.
   a. Start data collection.
   b. Empty and rinse the cuvette. Using the solution in Beaker 1, rinse the cuvette twice with ~1 mL amounts and then fill it 3/4 full. Wipe the outside with a tissue and place it in the device (Colorimeter or Spectrometer). Close the lid on the Colorimeter.
   c. When the value displayed on the screen has stabilized, Press "**collect" icon** located on the bottom left corner of the screen, then tap **Keep** and *enter the value for the concentration* **(in decimal form)** of $FeSCN^{2+}$ from your Pre-Lab calculations. Select **OK**. The absorbance and concentration values have now been saved for the first solution. **DO NOT PRESS THE "*STOP*" BUTTON (red) UNTIL STEP 8.** Record your absorbance and concentration data in your lab notebook as well.
   d. Discard the cuvette contents as directed by your instructor. Using the solution in Beaker 2, rinse the cuvette twice with ~1 mL amounts, and then fill it 3/4 full. Place the cuvette in the device, wait for the value displayed on the screen to stabilize, and tap **Keep**. Enter the value for the concentration of $FeSCN^{2+}$ in Beaker 2, next select **OK**.
   e. Repeat the procedure for Beakers 3 and 4. **Note:** Wait until Step 10 to test the unknown. Either press **"collect" icon** to end data gathering or the **RED square icon** to stop.

8. After stopping data collection, analyze the data immediately to verify precision of data. To examine the data pairs on the displayed graph, tap any data point. As you tap each data point, the absorbance and concentration values are displayed to the right of the graph. Record the absorbance and concentration data values in your notebook. If you want to discard a data point, (1) press on "table" icon, select "concentration" and set decimal places to 5, then press OK. (2) Search through data in the table, select the questionable data point, press "table" icon, and choose "strike through data". (3) "Restore data" will reverse the process.

9. Display a graph of absorbance *vs.* concentration with a linear regression curve.
   a. Choose **Graph Options** from the **Graph** menu.
   b. Select **Autoscale** from 0 and select **OK**.
   c. Choose **Curve Fit** from the **Analyze** menu.
   d. Select **Linear** as the Fit Equation. The linear-regression statistics for these two data columns are displayed for the equation in the form

$$y = mx + b$$

   e. Select **OK**. The graph should indicate a direct relationship between absorbance and concentration, a relationship known as Beer's law. The regression line should closely fit

the five data points *and* pass through (or near) the origin of the graph. Record the linear fit equation in your data table.

Part II Test an Unknown Solution of SCN^-

10. Obtain about 10 mL of the unknown SCN^- solution. Use a pipet to measure out 5.0 mL of the unknown into a clean and dry 100 mL beaker. Add precisely 5.0 mL of 0.200 M $Fe(NO_3)_3$ and 40.0 mL of distilled water to the beaker. Stir the mixture thoroughly.

11. Using the solution in the beaker, rinse a cuvette twice with ~1 mL amounts and then fill it 3/4 full. Place the cuvette of unknown in the device (Colorimeter).

12. Determine the concentration of the unknown SCN^- solution.

    a. Tap the **Meter** icon located on the top left-hand corner.
    b. Monitor the absorbance value. When this value has stabilized, record it in your data table.
    c. Tap the **Graph** tab. On the Graph screen, choose **Interpolate** from the **Analyze** menu. Tap any point on the regression curve (or use the ◄ or ► keys on LabQuest) to determine the concentration of your unknown SCN^- solution. Record the concentration in your data table.

Part III Prepare and Test Equilibrium Systems

13. Prepare four test tubes of solutions, according to the chart below. Repeat Steps 11 and 12 from Part II to test the absorbance values of each mixture. Record the test results in your data table. Record the $[FeSCN^{2+}]$ in the table in Data Analysis section #3. **Note**: You are using 0.0020 M $Fe(NO_3)_3$ in this test.

Test tube number	0.0020 M $Fe(NO_3)_3$ (mL)	0.0020 M SCN^- (mL)	H_2O (mL)
blank	3.00	0.00	7.00
1	3.00	2.00	5.00
2	3.00	3.00	4.00
3	3.00	4.00	3.00
4	3.00	5.00	2.00

REPORT SHEET EXPERIMENT 10 NAME: _____

PRE-LAB EXERCISE

For the solutions that you will prepare in Step 2 of Part I, calculate the [$FeSCN^{2+}$]. Presume that all of the SCN^- ions react. In Part I of the experiment, mol of SCN^- = mol of $FeSCN^{2+}$. Thus, the calculation of [$FeSCN^{2+}$] is: mol $FeSCN^{2+}$ ÷ L of *total* solution. Record these values in the table below. Show your calculations in your lab notebook.

Beaker number	[$FeSCN^{2+}$]
1	
2	
3	
4	
(blank)	0.00 M

POST-LAB REPORT

DATA TABLE FOR PARTS I & II

Beaker	Absorbance	[$FeSCN^{2+}$]
1		
2		
3		
4		
Unknown, Part II		

DATA TABLE FOR PART III

Test tube number	Absorbance
1	
2	
3	
4	

DATA ANALYSIS

1. (Part II) Use the calibration equation from Item 1 and the absorbance reading for your unknown solution to determine [SCN^-].

2. (Part II) Compare your experimental [SCN^-], of your unknown, with the actual [SCN^-]. Suggest reasons for the disparity.

3. (Part III) Use the absorbance values, along with the best fit line equation of the standard solutions in Part I to determine the [$FeSCN^{2+}$] at equilibrium for each of the mixtures that you prepared in Part III. Complete the table and give an example of your calculations below.

Test tube number	1	2	3	4
[$FeSCN^{2+}$]				

4. (Part III) Calculate the equilibrium concentrations for Fe^{3+} and SCN^- for the mixtures in Test Tubes 2–5 in Part III. Complete the table and give an example of your calculations.

Test tube number	1	2	3	4
[Fe^{3+}]				
[SCN^-]				

5. Calculate the value of K_{eq} for the reaction. Explain how you used the data to calculate K_{eq}.