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 K_{eq} 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.

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

computer	0.200 M iron (III) nitrate, $Fe(NO_3)_3$, solution in 1.0 M HNO_3
Vernier computer interface*	0.0020 M iron (III) nitrate, $Fe(NO_3)_3$, solution in 1.0 M HNO_3
Logger *Pro*	0.0020 M thiocyanate, SCN^{-}
Colorimeter or Spectrometer	potassium thiocyanate, KSCN solution of unknown concentration
plastic cuvette	distilled water
four 10.0 mL pipettes	50 mL volumetric flask
pipet pump or bulb	tissue
six 20 × 150 mm test tubes	Temperature Probe (optional)
test tube rack	
eight 100 mL beakers	
plastic Beral pipets	

* No interface is required if using a Spectrometer

PRE-LAB EXERCISE

For the solutions that you will prepare in Step 2 of Part I below, 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.

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

PROCEDURE

Part I Prepare and Test Standard Solutions

1. Obtain and wear goggles.

2. Label five 100 mL beakers 1-5. Obtain small volumes of 0.200 M $Fe(NO_3)_3$, 0.0020 M SCN^-, and distilled water. **CAUTION:** *$Fe(NO_3)_3$ solutions in this experiment are prepared in 1.0 M HNO_3 and should be handled with care.* Prepare four solutions according to the chart below (The fifth beaker is a blank.). Use a 10.0 mL pipet and a pipet pump or bulb to transfer each solution to a 50 mL volumetric flask. Mix each solution 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)	H_2O (mL)
1	5.0	5.0	40.0
2	5.0	4.0	41.0
3	5.0	3.0	42.0
4	5.0	2.0	43.0
blank	5.0	0.0	45.0

Note: The fifth beaker is prepared to be used as a blank for your spectrometer (or 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 with distilled water. 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.

Spectrometer Users Only (Colorimeter users proceed to the Colorimeter section)

4. Use a USB cable to connect the Spectrometer to the computer. Choose New from the File menu.

5. To calibrate the Spectrometer, place the blank cuvette into the cuvette slot of the Spectrometer, choose Calibrate → Spectrometer from the Experiment menu. The calibration dialog box will display the message: "Waiting 90 seconds for lamp to warm up." After 90 seconds, the message will change to "Warmup complete." Click OK.

6. Determine the optimum wavelength for the equilibrium mixture and set up the mode of data collection.
   a. Empty the water from the blank 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, place it in the Spectrometer.
   b. Click [Collect]. The absorbance *vs.* wavelength spectrum will be displayed. Note that one area of the graph contains a peak absorbance. Click [Stop].
   c. To save your graph of absorbance *vs*. wavelength, select Store Latest Run from the Experiment menu.
   d. Click the Configure Spectrometer Data Collection icon, , on the toolbar. A dialog box will appear.
   e. Select Absorbance *vs*. Concentration under Set Collection Mode. The wavelength of maximum absorbance (λ max) is automatically identified. Click [OK].
   f. Proceed directly to Step 7.

Colorimeter Users Only

4. Connect the Colorimeter to the computer interface. Prepare the computer for data collection by opening the file “10 Equilibrium” from the *Advanced Chemistry with Vernier* folder of Logger*Pro*.

5. Open the Colorimeter lid, insert the blank, and close the lid.

6. Calibrate the Colorimeter and prepare to test the standard solutions.
   a. Press the < or > button on the Colorimeter to select a wavelength of 470 nm (Blue).
   b. Press the CAL button until the red LED begins to flash and then release the CAL button.
   c. When the LED stops flashing, the calibration is complete.
   d. Empty the water from the blank 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, place it in the Colorimeter.

Both Colorimeter and Spectrometer Users

7. Collect absorbance-concentration data for the five standard equilibrium mixtures.
   a. Leave the cuvette, containing the Beaker 1 mixture, in the device (Colorimeter or Spectrometer). Close the lid on the Colorimeter.)
   b. Click [Collect]. Click [Keep], type the concentration of $FeSCN^{2+}$ (from your pre-lab calculations) in the edit box, and click [OK].
   c. Discard the cuvette contents as directed. Rinse and fill the cuvette with the solution in Beaker 2 and place it in the device. After the reading stabilizes, click [Keep], type the concentration of $FeSCN^{2+}$ (from your pre-lab calculations) in the edit box, and click [OK].
   d. Repeat Part b of this step to measure the absorbance of the solutions in Beakers 3, 4, and 5.
   e. Click [Stop] when you have finished collecting data. Click the Examine button, , and write down the absorbance values for each data pair in your data table.

8. Click the Linear Fit button, . A best-fit linear regression equation will be plotted for your data. This line should pass near or through the data points *and* the origin of the graph. Leave the equation in place on the graph and proceed to Step 9.

Part II Test an Unknown Solution of SCN^-

9. 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.

10. 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. Read the absorbance value displayed in the meter. (**Important:** The reading in the meter is live, so it is **not** necessary to click ▶ Collect to read the absorbance value.) When the displayed absorbance value stabilizes, record its value in your Data and Calculations table for Parts I and II.

11. Determine the concentration of the unknown SCN^- solution.
    a. Choose Interpolate from the Analyze menu. A vertical cursor now appears on the graph. The cursor's concentration and absorbance coordinates are displayed in the floating box.
    b. Move the cursor along the regression line until the absorbance value is approximately the same as the absorbance value you recorded in Step 10. The corresponding concentration value is the concentration of the unknown solution, in mol/L. Record the value in your Data Table for Parts I and II.

Part III Prepare and Test Equilibrium Systems

12. Prepare four test tubes of solutions, according to the chart below. Repeat Steps 10 and 11 from Part II to test the absorbance values of each mixture. Record the test results in your data table. **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)
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

DATA TABLE

Parts I and II

Beaker	Absorbance
1	
2	
3	
4	
Unknown, Part II	

Concentration Unknown	mol/L

Part III

Test tube number	Absorbance	Net absorbance
1		
2		
3		
4		

DATA ANALYSIS

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

2. (Part III) Use the net 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 below and give an example of your calculations.

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

3. (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 below 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}.

Vernier Lab Safety Instructions Disclaimer

THIS IS AN EVALUATION COPY OF THE VERNIER STUDENT LAB.

This copy does not include:

- **Safety information**
- **Essential instructor background information**
- **Directions for preparing solutions**
- **Important tips for successfully doing these labs**

The complete *Advanced Chemistry with Vernier* lab manual includes 35 labs and essential teacher information. The full lab book is available for purchase at: http://www.vernier.com/cmat/chema.html

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