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 use a colorimeter to help you measure the concentrations (see Figure 1). The amount of light absorbed by a colored solution is proportional to its concentration. The red $FeSCN^{2+}$ solution absorbs blue light, and it will be analyzed at 470 nm (blue light).

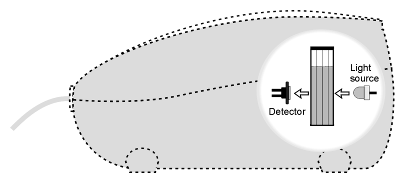

Figure 1

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

LabQuest
LabQuest App
Vernier Colorimeter
Temperature Probe (optional)
plastic cuvette
four 10.0 mL pipettes
pipet pump or bulb
six 20 × 150 mm test tubes
50 mL volumetric flask
eight 100 mL beakers
plastic Beral pipets

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^-
test tube rack
distilled water
tissue

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	0.00 M
2	
3	
4	
5	

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 five solutions according to the chart below. 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	0.0	45.0
2	5.0	2.0	43.0
3	5.0	3.0	42.0
4	5.0	4.0	41.0
5	5.0	5.0	40.0

3. Connect the Colorimeter to LabQuest and choose New from the File menu. If you have an older sensor that does not auto-ID, manually set up the sensor.

4. Calibrate the Colorimeter.
   a. Prepare a *blank* by filling an empty cuvette 3/4 full with distilled water.
   b. Place the blank in the cuvette slot of the Colorimeter and close the lid.
   c. Press the < or > buttons on the Colorimeter to set the wavelength to 470 nm (Blue). Then calibrate by pressing the CAL button on the Colorimeter. When the LED stops flashing, the calibration is complete.

5. On the Meter screen, tap Mode. Change the data-collection mode to Events with Entry. Enter the Name (Concentration) and Units (mol/L). Select OK.

6. You are now ready to collect absorbance data for the standard solutions. **Note**: Take readings within 4 minutes of preparing the mixtures.
   a. Start data collection.
   b. Empty the water from 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, place it in the Colorimeter, and close the lid. When the absorbance readings stabilize, tap Keep and enter the concentration of $FeSCN^{2+}$ (from your Pre-Lab exercise) for the first trial. Select OK to continue.
   c. Discard the cuvette contents as directed. Rinse and fill the cuvette with the solution in Beaker 2. Wipe the outside with a tissue, place it in the Colorimeter, and close the lid. Follow the procedure in Part b of this step to measure the absorbance and enter the concentration of this solution.
   d. Repeat this process to find the absorbance of the solutions in Beakers 3, 4, and 5.
   e. Stop data collection to view a graph of absorbance *vs.* concentration. To examine the data pairs on the displayed graph, select any data point. As you tap each point, the absorbance and concentration values of each data point are displayed to the right of the graph.

7. Record the absorbance values, for each of the five solutions, in your data table.

8. Display a graph of absorbance vs. concentration with a linear regression curve.
   a. Choose Curve Fit from the Analyze menu.
   b. Select Linear as the Fit Equation. The linear-regression statistics are displayed to the right of the graph for the equation in the form

$$y = mx + b$$

   where *x* is time, *y* is absorbance, *m* is the slope, and *b* is the y-intercept.
   c. Record the best-fit line equation in your data table and select OK.

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 test tube, rinse a cuvette twice with ~1 mL amounts and then fill it 3/4 full. Wipe the outside with a tissue, place it in the Colorimeter, and close the lid.

11. Determine the concentration of the unknown.
    a. Tap Meter. Monitor the absorbance readings on the screen.
    b. When the readings stabilize, record the absorbance value for your unknown in your data table.
    c. Remove and clean the cuvette.
    d. Tap Graph and choose Interpolate from the Analyze menu.
    e. Trace the linear regression equation to find the concentration of your unknown at the absorbance displayed on the meter.

LabQuest 10

Part III Prepare and Test Equilibrium Systems

12. Prepare five test tubes of solutions according to the chart below. Follow the necessary steps from Part I to test the absorbance values of each mixture. Record the 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	0.00	7.00
2	3.00	2.00	5.00
3	3.00	3.00	4.00
4	3.00	4.00	3.00
5	3.00	5.00	2.00

13. To get good data for the calculation of K_{eq}, you must determine the net absorbance of the solutions in Test Tubes 2–5. To do this, subtract the absorbance reading for Test Tube 1 from the absorbance readings of Test Tubes 2–5, and record these values as net absorbance in your data table.

DATA TABLE

Parts I and II

Beaker number	Absorbance
1	
2	
3	
4	
5	
Unknown, Part II	

Best-fit line equation for the Part I standard solutions: ______________________________

Part III

Test tube number	Absorbance	Net absorbance
1		
2		
3		
4		
5		

DATA ANALYSIS

1. (Part II) Use the best-fit line 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 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	2	3	4	5
[$FeSCN^{2+}$]				

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 below and give an example of your calculations.

Test tube number	2	3	4	5
[Fe^{3+}]				
[SCN^-]				

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