Experiment: The Determination of K_{eq} for $FeSCN^{2+}$

Introduction

For any reversible chemical reaction at equilibrium, the concentrations of all reactants and products are constant or stable. There is no further net change in the amounts of reactants and products unless the reaction mixture is disturbed in some way. The equilibrium constant provides a mathematical description of the position of equilibrium for any reversible chemical reaction.

Background

Any reversible reaction eventually reaches a position of *chemical equilibrium*. In some cases, equilibrium favors products and it appears that the reaction proceeds essentially to completion. The amount of reactants remaining under these conditions is very small. In other cases, equilibrium favors reactants and it appears that the reaction occurs only to a slight extent. Under these conditions, the amount of products present at equilibrium is very small.

These ideas can be expressed mathematically in the form of the equilibrium constant. Consider the following general equation for a reversible chemical reaction:

$$aA + bB \rightleftharpoons cC + dD \qquad \text{Equation 1}$$

The *equilibrium constant* K_{eq} for this general reaction is given by Equation 2, where the square brackets refer to the molar concentrations of the reactants and products at equilibrium

$$K_{eq} = \frac{[C]^c\,[D]^d}{[A]^a[B]^b} \qquad \text{Equation 2}$$

The equilibrium constant gets its name from the fact that for any reversible chemical reaction, the value of K_{eq} is a constant at a particular temperature. The concentrations of reactant and products at equilibrium vary, depending on the initial amounts of materials present. The special ratio of reactants and products described by K_{eq} is always the same as long as the system has reached equilibrium and the temperature does not change. The value of K_{eq} can be calculated if the concentrations of reactants and products at equilibrium are known.

The reversible chemical reaction of iron(III) ions, Fe^{3+} with thiocyanate ion, SCN^-, provides a convenient example for determining the equilibrium constant of a reaction. As shown in Equation 3, Fe^{3+} and SCN^- ions combine to form a special type of combined or "complex" ion having the formula $FeSCN^{2+}$.

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons Fe(SCN)^{2+}(aq) \qquad \text{Equation 3}$$

The equilibrium constant expression for this reaction is given in Equation 4.

$$K_{eq} = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^{-}]} \qquad \text{Equation 4}$$

The value of K_{eq} can be determined experimentally by mixing known concentrations of Fe^{3+} and SCN^{-} ions and measuring the concentration of $FeSCN^{2+}$ ions at equilibrium. The reactant ions are pale yellow and colorless, respectively, while the product ions are blood-red. The concentration of $FeSCN^{2+}$ complex ions at equilibrium is proportional to the intensity of the red color.

A special sensor called a colorimeter will be used to measure the absorbance of light by the red ions. The more intense the red color, the greater the absorbance. The wavelength of light absorbed by the red ions is about 438 nm. None of the other ions present in solution absorb light at this wavelength. As long as the same size container is used to measure the absorbance of each solution, the absorbance is directly proportional to the concentration of $FeSCN^{2+}$ ions.

In Part A, you will prepare a series of **standard solutions** that contain known concentrations of $[Fe(SCN)]^{2+}$ and will determine their absorbance at 468 nanometers. The concentrations and absorbance values will be used to construct a calibration graph or a **standard curve** for $[Fe(SCN)]^{2+}$.

In Part B of the experiment, various combinations of $Fe(NO_3)_3$ and KSCN will be combined. The amount of product formed, $[Fe(SCN)]^{2+}$, will be determined from the standard curve prepared in part one. From the original amounts of reactants for each trial and the amount of product formed, the concentration of all species at equilibrium may be determined. When these concentrations are substituted into the equation for the equilibrium constant, values for the equilibrium constant are determined. An average value for the constant will be determined.

Purpose: To determine the equilibrium constant for the reaction of iron(III) ions with thiocyanate ions.

Equipment & Chemicals

- 0.0020 M $Fe(NO_3)_3$
- 0.200 M $Fe(NO_3)_3$
- 0.0020 M KSCN
- 0.00020 M KSCN
- colorimeter with cuvettes
- thermometer probe
- GLX Interface
- 10 small test tubes
- permanent maker
- 3-pipets
- pipet fillers
- lint free paper
- wash bottle

Safety
Wear goggles & your lab coat!

The iron(III) nitrate solution contains 1 M HNO_3 is a corrosive liquid; it will stain skin and clothing. Notify Mrs. Lowder and clean up any spills immediately. KSCN is toxic by ingestion; it can generate poisonous hydrogen cyanide gas if heated strongly. Avoid contact of all chemical with eyes and skin. Wash hands thoroughly with soap and water before leaving the laboratory.

Procedure
Part A: Preparing the Standard Solutions

1. Plug in the GLX and turn on. Connect the colorimeter in Port 1. Follow the instructions to select an absorbance of 468 nm. Use distilled water as a blank. The absorbance of the blank should be 0.

2. Obtain ten test tubes and label them #1-10.

3. The chart below provides the volumes of reactants needed to prepare the standard solutions. Notice that the concentration of the iron solution is much greater than that of the KSCN solution. This is to ensure that all of the KSCN is used up in the reaction. The concentration of the product will be determined from the volume and concentration of the KSCN used in each trial.

   Using a *separate pipet for* each reagent to be added, combine the following volumes of reagents to prepare the test solutions. Use a stirring rod to mix each solution. Rinse the stirring rod and dry it between solutions. NOTE: There are two different stock solutions of $Fe(NO_3)_3$. Read the labels carefully before use!

Part A: Standard Solutions

Test Solution	0.200 M $Fe(NO_3)_3$	0.00020 M KSCN
#1	8.00 mL	2.00 mL
#2	7.00 mL	3.00 mL
#3	6.00 mL	4.00 mL
#4	5.00 mL	5.00 mL
#5	4.00 mL	6.00 mL

Part B: Equilibrium Solutions

4. Use a pipet to measure the volumes of the reactants listed in the table below. Note that this set of combinations uses a more dilute $Fe(NO_3)_3$ solution. Be sure to read the reagent labels carefully before use. Be sure to use a clean pipette for each type of solution. Mix each solution using a stirring rod. Rinse the stirring rod and dry it between solutions.

5. Measure the temperature of one of the solutions and record it in the Part B Data Table.

Part B: Equilibrium Solutions

Test Solution	0.0020 M $Fe(NO_3)_3$	0.0020 M KSCN	Deionized Water
#6	5.00 mL	1.00 mL	4.00 mL
#7	5.00 mL	2.00 mL	3.00 mL
#8	5.00 mL	3.00 mL	2.00 mL
#9	5.00 mL	4.00 mL	1.00 mL
#10	5.00 mL	5.00 mL	0

Colorimetry Measurements

1. Fill each cuvette with approximately 6 mL of the test solutions #1-5 and fill one cuvette with water. The cuvette with water will be called the blank. Wipe the outside of each cuvette with lint free paper.

2. Turn on the GLX and connect the colorimeter to Port 1. A graph should be displayed. Go to the home screen and select the digital reading. Using the check mark, highlight the heading and press the check mark again. Select Blue (468 nm) Absorbance for one reading and Blue (468 nm) Transmittance for the other reading.

3. To calibrate the colorimeter insert the blank with the arrow on the cap lined up with the screw on the colorimeter. Shut the lid tightly. Press the green button on the colorimeter. Once the light on the green button has gone out, remove the cuvette. The Blue (468 nm) Transmittance should be 100%.

4. Insert the cuvette containing Test Solution #1. Handle the cuvettes by their tops to avoid getting fingerprints on the surface. Wipe the cuvettes with lint-free tissue paper. Remove the cuvette from the colorimeter and replace it with the cuvette containing test solution #2. Be sure that the arrow on the lid is lined up with the screw on the colorimeter. Press the play button and record the Absorbance value in the data tables.

5. Repeat this procedure for all test solutions #2-10. Be sure to rinse and dry the cuvette when you switch solutions. Dispose of all waste products in the hood. When finished, rinse all cuvettes with distilled water.

6. Construct a calibration curve for the data collected in Step 4. Plot absorbance on the y-axis and concentration of [$Fe(SCN)^{2+}$] on the x-axis. Draw a best-fit line through the data points. This graph will be used to determine the amount of product formed in Part B.

7. When the absorbance reading stabilizes, record the absorbance measurement in Part B data table.

8. Using your calibration graph, determine the concentration of [$Fe(SCN)^{2+}$] for each of the trials. Record in Part B data table.

9. Measure the temperature of each of the solution and record it in the data table. Be sure to rinse the thermometer between solutions and dry it. Average the temperatures. The average will be assumed to be the equilibrium temperature for all the solutions.

10. Dispose of your waste in the hood. Rinse the cuvettes with deionized water and dry with lint free paper.

Data Table
Part A: Standard Solutions

$[SCN^-] = [Fe(SCN)^{2+}]$

Test Solution	$[Fe^{3+}]_o$	$[SCN^{1-}]_o$	$[FeSCN^{2+}]$	Absorbance
#1				
#2				
#3				
#4				
#5				

Part B: Equilibrium Solutions

Temperature: ______________

Test Solution	6	7	8	9	10
Absorbance					
$[Fe(SCN)^{2+}]_{eq}$ from graph					
$[Fe^{3+}]_o$ initial					
$[Fe^{3+}]_{eq}$ final					
$[SCN^-]_o$ initial					
$[SCN^-]_{eq}$ final					
K_{eq}					

Analysis:

1. Determine initial amounts of [Fe^{3+}] and [SCN^-] in Part A & B by using the dilution equation $M_1V_1 = M_2V_2$.
   For Test Solution #1:
   M_1 = concentration of solution before mixing
   V_1 = volume of the solution before mixing
   V_2 = final volume of the test solution after mixing
   M_2 = the concentration of Fe^{3+} after mixing.

   Calculate [Fe^{3+}] for all ten test solutions.

   Use the dilution equation to calculate the concentration of SCN^- ions in the test solutions before any reaction occurs.

   Enter these values in the both data tables.

2. In Part A, the reaction uses all the SCN^- so the concentration of SCN^- is equal to the complex ion formed, $FeSCN^{2+}$. Enter these values in Part A data table.

3. Plot molar concentration of $FeSCN^{2+}$ versus absorbance for test solutions #1-5. Draw the line of best fit and include the equation for the line.

4. The unknown concentration of $FeSCN^{2+}$ ions in each test solution #6-10 can be determined from the graph. Find the absorbance value of the test solutions #6-10 on the graph and record the concentration of $[FeSCN^{2+}]_{eq}$ in Part B Data Table.

5. Calculate the equilibrium concentration of Fe^{3+} ions in each solution #6-10: subtract the equilibrium concentration of $FeSCN^{3+}$ ions from the initial concentration of Fe^{3+} ions. Enter the results in Part B Data Table
   $$[Fe^{3+}]_{eq} = [Fe^{3+}]_o – [FeSCN^-]_{eq}$$

6. Calculate the equilibrium concentration of SCN^- ions in each test solution #6-10. Subtract the equilibrium concentration of $Fe(SCN)^{2+}$ ions from the initial concentration of SCN^- ions. Enter the results in the data table for Part B.
   $$[SCN^-]_{eq} = [SCN^-]_o\text{-}[FeSCN^{2+}]_{eq}$$

7. Use the equilibrium expression to calculate K_{eq} for each trial and enter the results in the Part B data table.

8. Calculate the mean of the equilibrium constant.