

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

Introduction

There are many reactions that take place in solution that are equilibrium reactions; that is, they do not go to completion, both the forward and reverse reaction are occurring, and both reactants and products are always present. Examples of this type of reaction include weak acids such as acetic acid dissociating in water, weak bases such as ammonia reacting with water, and the formation of "complex ions" in which a metal ion combines with one or more negative ions. A reaction involving the formation of a complex ion which occurs when solutions of iron(III) are combined with solutions of the negative thiocyanate ion will be studied and the equilibrium constant determined.

Concepts

- Chemical equilibrium
- Equilibrium constant
- Complex-ion reaction
- Colorimetry

Background

Chemical reactions are driven to completion by two forces: a decrease in energy (exothermic reaction), or an increase in entropy. If both an energy decrease and an entropy increase occur in the forward reaction, the reaction will go to completion. An example of this type of reaction is the burning of ethane. The reaction is exothermic and has an increase in entropy, and it goes to completion.

However, when an energy decrease drives a reaction in one direction and an entropy increase drives it in the reverse direction, equilibrium will result. The reaction will not go to completion, but will reach a point where both reactants and products are present in a fixed ratio of concentration. The reaction will continue at the same rate in both forward and reverse directions, and the concentrations of products and reactants will stay constant.

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

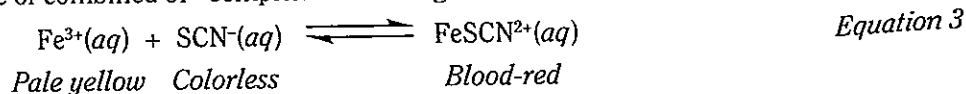


The *equilibrium constant* K_{eq} for this general reaction is given by Equation 2, where the square brackets refer to the molar concentrations of the reactants and products at equilibrium.

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

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 reactants 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 ions (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 $FeSCN^{2+}$.



Experiment 13

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

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

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. As noted in Equation 3, 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.

Compounds that are colored absorb a part of the visible spectrum of light. If a compound absorbs green light, it will appear red in color, the complementary color to green. A spectrophotometer is an instrument that measures the amount of light of a given wavelength or color that is absorbed by a solution.

A visible spectrophotometer consists of several components. First a source of visible light is needed. Next, a prism or diffraction grating and lenses are used to select light of a given wavelength and pass it through the solution. A sample holder, usually a test tube or cuvet is used to hold the solution. Next a photo tube or device to measure the amount of light that comes through the solution is needed. The last component is a meter to display the amount of light transmitted or absorbed by the solution.

To use the spectrophotometer, the desired wavelength must be selected, insert the sample inserted in the light path, and the amount of light absorbed or transmitted read. A colorimeter is a similar device that uses a color filter in place of the prism or diffraction grating. Both a colorimeter and spectrophotometer can determine the concentration of a colored solution using Beer's law.

Beer's law is a mathematical relation that is stated:

$$A = \epsilon b C$$

In Beer's law, the term "A" is the absorption of light. The term "ε" is the absorptivity of the sample. This is a value that indicates how much light of a given wavelength is absorbed by a given substance. If a substance has a very intense color, it will have a high absorptivity. The term "b" is the cell path. This is the width of the cell path (test tube) or cuvet through which the light passes. The term "C" is the molar concentration of the substance absorbing the light. When a substance is analyzed the absorptivity of the sample is constant, and the width of the cell path (test tube) does not change. Therefore, the absorption read by the spectrophotometer is directly proportional to the concentration of the sample. A graph of absorption versus concentration is a straight line.

Experiment Overview

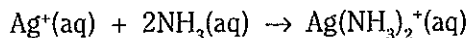
The purpose of this experiment is to calculate the equilibrium constant for the reaction of iron(III) ions with thiocyanate ions. The reaction is tested under different conditions to determine if the equilibrium constant always has the same numerical value. There are two parts to the experiment.

In Part 1, a series of reference solutions and test solutions are prepared. The reference solutions are prepared by mixing a large excess of Fe^{3+} ions with known amounts of SCN^- ions. According to LeChâtelier's Principle, the large excess of iron(III) ions should effectively convert all of the thiocyanate ions to the blood-red FeSCN^{2+} complex ions. The concentration of FeSCN^{2+} complex ions in the reference solutions is essentially equal to the initial concentration of SCN^- ions. The test solutions are prepared by mixing a constant amount of Fe^{3+} ions with different amounts of SCN^- ions. These solutions contain unknown concentrations of FeSCN^{2+} ions at equilibrium.

In Part 2, the absorbances of both the reference solutions and the test solutions are measured by colorimetry. A calibration curve is constructed from the absorption values of the reference solutions. The unknown concentrations of FeSCN^{2+} in the test solutions are calculated by comparing their absorbance readings to the absorbance values of the calibration curve. These values are used to determine the equilibrium concentrations and the equilibrium constant for the reaction.

Pre-Lab Questions Use a separate sheet of paper to answer the following questions.)

- Define equilibrium.
- The reaction for the formation of the diamminesilver ion is as follows:



- Write the equilibrium constant expression for the reaction.
 - An experiment was carried out to determine the value of the equilibrium constant, K_{eq} for the reaction

Total moles of Ag^+ present	3.6×10^{-3} moles
Total moles of NH_3 present	6.9×10^{-3} moles
Measured concentration of $\text{Ag}(\text{NH}_3)_2^+$ at equilibrium	3.4×10^{-2} M
Total solution volume	100 mL

 Calculate the equilibrium concentration of Ag^+ (uncomplexed).
 Calculate the equilibrium concentration of NH_3 (uncomplexed).
 Calculate the value of the equilibrium constant.
- “The equilibrium concentration of FeSCN^{2+} ions in each reference solution listed below is essentially equal to the concentration of SCN^- ions in solution before any reaction occurs.” Use LeChâtelier’s Principle to explain why this statement is true.
 - The five reference solutions in Part 1 are prepared by mixing 0.200 M $\text{Fe}(\text{NO}_3)_3$ solution and 0.00020 M KSCN solution in the amounts listed in the following table.

Standard	Volume of 0.200 M $\text{Fe}(\text{NO}_3)_3$ Solution	Volume of 0.00020 M KSCN Solution
Reference solution #1	8.0 mL	2.0 mL
Reference solution #2	7.0 mL	3.0 mL
Reference solution #3	6.0 mL	4.0 mL
Reference solution #4	5.0 mL	5.0 mL
Reference solution #5	4.0 mL	6.0 mL

The concentration of Fe^{3+} ions in the first reference solution (M_2) before any reaction occurs can be calculated using the so-called “dilution equation,” as shown below.

$$M_1V_1 = M_2V_2 \quad \text{Dilution Equation}$$

M_1 = concentration of solution before mixing = 0.200 M $\text{Fe}(\text{NO}_3)_3$

V_1 = volume of solution before mixing = 8.0 mL

V_2 = final volume of reference solution after mixing = 8.0 mL + 2.0 mL = 10.0 mL

$$M_2 = \frac{M_1V_1}{V_2} = \frac{(0.200 \text{ M})(8.0 \text{ mL})}{(10.0 \text{ mL})} = 0.16 \text{ M}$$

Use the dilution equation to calculate the concentration of SCN^- ions in the five reference solutions before any reaction occurs. Enter these values in Data Table 1 as $[\text{FeSCN}^{2+}]$.

Experiment 13

5. The following table summarizes the volumes of Fe^{3+} and SCN^- stock solutions that will be mixed together to prepare the test solutions in Part 1. Use the dilution equation to calculate the concentrations of Fe^{3+} and SCN^- ions in each test solution before any reaction occurs. Enter the results of these calculations in scientific notation in Data Table 2. *Hint:* The final volume (V_2) of each test solution is 10.0 mL.

Sample	Volume of 0.0020 M $\text{Fe}(\text{NO}_3)_3$ Solution	Volume of 0.00020 M KSCN Solution	Volume of Distilled Water Added
Test solution #6	5.0 mL	1.0 mL	4.0 mL
Test solution #7	5.0 mL	2.0 mL	3.0 mL
Test solution #8	5.0 mL	3.0 mL	2.0 mL
Test solution #9	5.0 mL	4.0 mL	1.0 mL
Test solution #10	5.0 mL	5.0 mL	0 mL

Materials

Chemicals

Iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3$, 0.200 M, 30 mL[†]

Iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3$, 0.0020 M, 25 mL[†]

Potassium thiocyanate, KSCN, 0.0020 M, 15 mL

Potassium thiocyanate, KSCN, 0.00020 M, 20 mL

Water, distilled or deionized

Equipment

Beakers or large test tubes, 50-mL, 10

Colorimeter sensor or spectrophotometer

Cuvets, 6

Labeling or marking pen

Pipet bulb or pipet filler

Pipets, serological-type, 5- or 10-mL, 5

Stirring rod

Thermometer

Tissues or lens paper, lint-free

Wash bottle

[†]Contains 1 M nitric acid as the solvent.

Safety Precautions

Iron(III) nitrate solution contains 1 M nitric acid and is a corrosive liquid; it will also stain skin and clothing. Notify the teacher and clean up all spills immediately. Potassium thiocyanate is toxic by ingestion; it can generate poisonous hydrogen cyanide gas if heated strongly. Avoid contact of all chemicals with eyes and skin. Wear chemical splash goggles and chemical-resistant gloves and apron. Wash hands thoroughly with soap and water before leaving the laboratory.

Procedure

Part 1. Preparing the Solutions

1. Obtain ten 50-mL beakers or large test tubes.
2. Prepare the five reference solution test tubes or beakers listed in the table below. Use a separate pipet to transfer the appropriate volumes of each reagent. Mix each solution using a stirring rod. Rinse the stirring rod and dry it between solutions. Label the test tubes or beakers with the corresponding reference solution number.

Standard	Volume of 0.200 M $\text{Fe}(\text{NO}_3)_3$ Solution	Volume of 0.00020 M KSCN Solution
Reference solution #1	8.0 mL	2.0 mL
Reference solution #2	7.0 mL	3.0 mL
Reference solution #3	6.0 mL	4.0 mL
Reference solution #4	5.0 mL	5.0 mL
Reference solution #5	4.0 mL	6.0 mL

3. Using a separate pipet for each reagent to be added, combine the following volumes of reagents to prepare the test solutions. *Note:* Label the tubes with the corresponding solution numbers 6 through 10. Read the reagent labels carefully before use!

Sample	Reagents		
	0.0020 M $\text{Fe}(\text{NO}_3)_3$	0.0020 M KSCN	Distilled Water
Test solution #6	5.0 mL	1.0 mL	4.0 mL
Test solution #7	5.0 mL	2.0 mL	3.0 mL
Test solution #8	5.0 mL	3.0 mL	2.0 mL
Test solution #9	5.0 mL	4.0 mL	1.0 mL
Test solution #10	5.0 mL	5.0 mL	0 mL

4. 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 Data Table 2. This will be used as the equilibrium temperature for all of the solutions.

Part 2. Colorimetry Measurements

- Follow the procedure for your colorimetric measurements of the solution as directed by the teacher. Generally, spectrophotometers are used as follows: Turn the instrument on and allow it to warm up for 15 minutes. Set the wavelength at 450 nm. With no light passing through the instrument to the phototube, set the percent transmittance to zero with the "zero" control. Handle cuvetts at the top so no fingerprints are in the light path. Clean cuvetts with a tissue. Place a cuvette which is about 2/3 full of distilled water into the sample holder and set the percent transmittance to 100% with the appropriate control (not the zero control). Fill a cuvette about 2/3 full of a test solution, place it in the spectrophotometer and read the absorbance. Consult the instrument manual for details on its use.
- Measure the absorbance of each of the reference solutions at 450 nm, using distilled water as the zero absorbance reference in the spectrophotometer. If absorbance is difficult to measure precisely on the meter because it is in the high range where the numbers are close together, measure percent transmittance and calculate the absorbance for each solution. Absorbance = $-\log T$, where T is transmittance expressed as a decimal. Record the absorbance value for each reference solution used in Data Table 1.
- Repeat steps 1 and 2 for each of the test solutions. Record the absorbances in Data Table 2.
- Dispose of the contents of the cuvetts and of the remaining test solutions as directed by your teacher. Follow your teacher's directions for rinsing and drying the cuvetts.

Disposal and Cleanup

Your teacher will provide disposal and cleanup instructions.

Experiment 13

Data Tables

Data Table 1 — Reference Solutions

Temperature		
Sample	[FeSCN ²⁺]	Absorbance
Reference solution #1		
Reference solution #2		
Reference solution #3		
Reference solution #4		
Reference solution #5		

Data Table 2 — Test Solutions

Temperature			
Sample	[Fe ³⁺]*	[SCN ⁻]*	Absorbance
Test solution #6			
Test solution #7			
Test solution #8			
Test solution #9			
Test solution #10			

*These are the concentrations of ions in solution immediately after mixing and before any reaction has occurred. See the *Pre-Lab Questions* for calculations.

Data Table 3 — Results

Sample	[FeSCN ²⁺] _{eq}	[Fe ³⁺] _{eq}	[SCN ⁻] _{eq}	<i>K</i> _{eq}
Test Solution #6				
Test Solution #7				
Test Solution #8				
Test Solution #9				
Test Solution #10				
Average value				
Average deviation				

Post-Lab Calculations and Analysis

(Use a separate sheet of paper to answer the following questions.)

1. On graph paper, plot molar concentration of FeSCN^{2+} versus absorbance as shown in Figure 1, and draw the best-fitting straight line through the data points. Include the origin (zero absorbance for zero concentration) as a valid point.

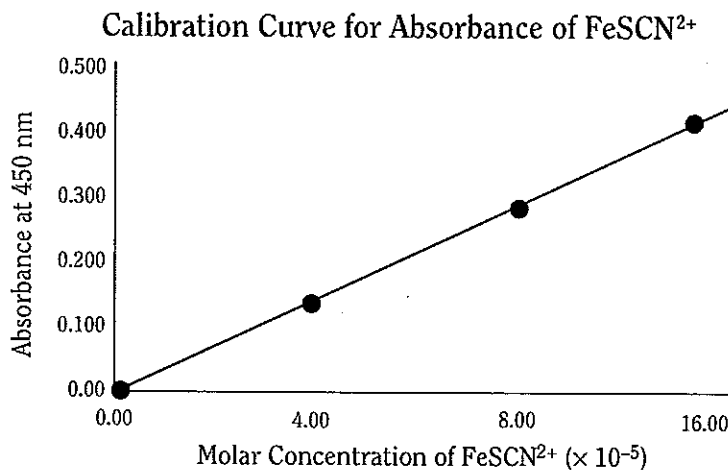


Figure 1. Sample Graph of Absorbance versus Concentration of FeSCN^{2+}

2. The unknown concentration of FeSCN^{2+} ions in each test solution can be determined from the graph. Find the absorbance value of the test solution, read across to the best-fit, straight-line curve, and then down to the x -axis to find the concentration.
3. Record the FeSCN^{2+} concentration for each test solution in Data Table 3.
4. Calculate the equilibrium concentration of Fe^{3+} ions in each test solution #6–10: subtract the equilibrium concentration of FeSCN^{2+} ions from the initial concentration of Fe^{3+} ions (see the Test Solutions Data Table). Enter the results in Data Table 3.

$$[\text{Fe}^{3+}]_{\text{eq}} = [\text{Fe}^{3+}]_{\text{initial}} - [\text{FeSCN}^{2+}]_{\text{eq}}$$

5. Calculate the equilibrium concentration of SCN^- ions in each test solution #6–10: subtract the equilibrium concentration of FeSCN^{2+} ions from the initial concentration of SCN^- ions (Data Table 2). Enter the results in Data Table 3.

$$[\text{SCN}^-]_{\text{eq}} = [\text{SCN}^-]_{\text{initial}} - [\text{FeSCN}^{2+}]_{\text{eq}}$$

6. Use Equation 4 in the *Background* section to calculate the value of the equilibrium constant K_{eq} for each test solution #6–10. Enter the results in Data Table 3.
7. Calculate the *mean* (average value) of the equilibrium constant for the five test solutions.
8. Calculate the *average deviation* for K_{eq} : Find the absolute value of the difference between each individual value of the equilibrium constant and the mean. The average of these differences for solutions #6–10 is equal to the average deviation.
9. The average deviation describes the precision of the results. Does the precision indicate that the equilibrium constant is indeed a “constant” for this reaction? Explain.
10. Describe the possible sources of error in this experiment and their likely effect on the results.

Experiment 13

Post-Lab Questions *(Use a separate sheet of paper to answer the following questions.)*

1. Explain what is meant by an equilibrium constant. Was the value constant for all your experiments? Should it be constant?
2. What does the calculated value of the equilibrium constant, K_{eq} , indicate regarding the degree of completeness of the reaction? In other words, at equilibrium, are there mostly products, reactants, or relatively large amounts of both?
3. Explain what a spectrophotometer is and what it measures. Describe how the "standard" solutions were obtained and used to determine concentrations of unknown solutions.
4. When you use a spectrophotometer, should you set the wavelength of light to be the same color as that of the solution, or would a different color be more appropriate? Explain. What was the color of light chosen for this experiment? What was the color of the $FeSCN^{2+}$ complex ion?
5. What degree of precision (how many significant figures) can you obtain with the spectrophotometer that was used? What is the major source of error in the experiment?
6. Suggest other experiments in which a spectrophotometer would be useful.