

Evaluating the Equilibrium Constant for the Reaction of Iron(III) Ion with Thiocyanate Ion

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Purpose of the Experiment

Use spectrophotometric techniques to evaluate the equilibrium constant for the reaction of iron(III) ion with thiocyanate ion. Determine the equilibrium constants for five equilibrium mixtures prepared using solutions of these two ions with varying concentrations. Compare the five constants to determine a mean equilibrium constant for this reaction. Treat reaction mixtures for safe disposal.

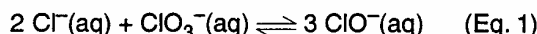
Background Information

Chemists often need to be able to predict the mass of products that could form from the reactants in a particular chemical reaction. To do so, we often employ a limiting reagent calculation. These calculations are based on the following assumptions: that the chemical reaction goes to completion, and that the reaction proceeds until the limiting reagent is completely converted into products.

These calculations often produce inaccurate results. This is because, rather than proceeding to completion, many reactions are **reversible**. In reversible reactions, while reactants are forming products, some of the products are reverting into reactants. We symbolize reversibility in chemical equations using double arrows (\rightleftharpoons).

In reversible reactions, the rate of the forward reaction depends on the concentrations of reactants; the rate of the reverse reaction depends on the concentrations of the products. At first, the high reactant concentrations cause a rapid forward reaction. As the forward reaction proceeds, however, reactant concentrations decrease as reactants change into products. Therefore, the forward reaction rate gradually decreases. At the same time, the increasing product concentrations cause the reverse reaction rate to increase. Eventually, the **rates** of the forward and reverse reactions become equal. Reactants become products just as rapidly as products change back into reactants. There is no further change in the concentrations of either reactants or products. At this point, we say that the reaction has achieved a **state of dynamic equilibrium** or simply that the reaction is **at equilibrium**.

Consider the reaction shown in Equation 1.

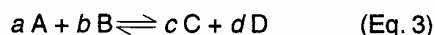


Regardless of the initial concentrations of reactants or product in this reaction, once the reaction is at equilibrium, the molar concentrations of all three substances will be fixed in the ratios represented by the expression in Equation 2. We refer to this expression as the **equilibrium constant expression** for the reaction. K_{eq} is the **equilibrium constant** for the reaction.

$$K_{\text{eq}} = \frac{[\text{ClO}^-]^3}{[\text{Cl}^-]^2 [\text{ClO}_3^-]} \quad (\text{Eq. 2})$$

The square brackets in Equation 2 symbolize the molar concentration, (M , or mol L^{-1}), of each indicated substance. Notice that the product concentration appears in the numerator of the expression, and the reactant concentrations appear in the denominator. Each concentration term is raised to the power of its coefficient in the balanced equation.

We use mathematical expressions similar to Equation 2 to describe the equilibrium constants, or equilibria, of all reversible chemical reactions. Consider the general reaction by Equation 3, with capital letters representing formulas and lowercase italic letters representing coefficients. The equilibrium constant expression for this reaction is shown in Equation 4.

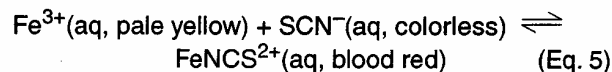


$$K_{\text{eq}} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (\text{Eq. 4})$$

Equilibrium constants are useful because, based on the magnitude of K_{eq} , we can determine whether an equilibrium mixture consists primarily of reactants, products, or relatively equal molar amounts of each. Because the value of K_{eq} for each reaction varies slightly with reaction temperature, we must reference any equilibrium constant with the temperature at which it was measured.

Forming the Isothiocyanatoiron(III) Ion

In acidic solution, iron(III) ion (Fe^{3+} , or ferric ion) reversibly bonds to thiocyanate ion (SCN^-), forming a blood-red coordination ion, as shown in Equation 5. Some scientists write the product formula as FeSCN^{2+} . However, there is evidence that the new covalent bond actually forms between the iron and the nitrogen atoms, making the formula FeNCS^{2+} more accurate. FeNCS^{2+} ion is called isothiocyanatoiron(III) ion.



For this experiment, we use a solution of iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3$, as a source of Fe^{3+} ions. A solution of sodium thiocyanate, NaSCN , serves as the SCN^- ion source. Studies show that the K_{eq} for a reaction is somewhat dependent on the total ionic concentration of the equilibrium mixture. Therefore, we prepare all solutions using $0.10M$ nitric acid (HNO_3) solution as a solvent, rather than water, to ensure that all mixtures have comparable ionic strength.

Spectrophotometrically Measuring the FeNCS^{2+} Ion Concentration

Because dissolved FeNCS^{2+} ions form an intensely colored solution, we can conveniently measure their concentration with an instrument known as a **spectrophotometer**. Using this instrument, we can cause light of a selected wavelength to pass through a sample of the equilibrium mixture. The colored solution absorbs some of the light. This absorption decreases the intensity of light reaching a detector, leading to a measurement of **absorbance**, A . When the wavelength of the light and its path length through the solution are kept constant, the measured absorbance is directly proportional to the molar concentration of the absorbing species, in this case FeNCS^{2+} , in solution.

The equation relating absorbance and molar concentration (c), known as **Beer's Law**, is shown in Equation 6.

$$A = \epsilon bc \quad (\text{Eq. 6})$$

In Equation 6, ϵ is the **molar absorptivity coefficient**, which indicates how efficiently the absorbing species absorbs light of the chosen wavelength; b is the path length, in centimeters, of the light passing through the solution.

A spectrophotometer is designed to display measured data using two scales. The amount of light absorbed by the solution is indicated by an absorbance reading. The instrument also displays a percent transmittance ($\%T$) reading, which indicates the amount of light passing through the solution and reaching the detector. The design of some spectrophotometers allows us to read $\%T$ more precisely than A . In this experiment, we will measure $\%T$ and convert the reading to the equivalent absorbance, using Equation 7.

$$A = 2.000 - \log(\%T) \quad (\text{Eq. 7})$$

We can determine the FeNCS^{2+} ion concentrations in the equilibrium mixtures using their absorbance data and a calibration plot known as a **Beer's Law plot**. Because absorbance is directly proportional to the molar concentration of the absorbing species, we can expect such a plot to be linear and pass through the origin (0,0). A typical Beer's Law plot is shown in Figure 1.

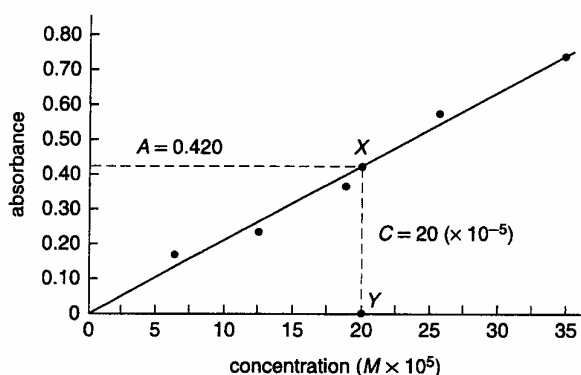


Figure 1 A Beer's Law plot

Preparing a Beer's Law Plot for FeNCS^{2+} Ion

To prepare a Beer's Law plot, we begin by measuring the % T of a series of solutions of various known FeNCS^{2+} ion concentrations. Then we calculate the equivalent absorbance of each solution, using Equation 7. Finally, we plot absorbance against molar concentration of FeNCS^{2+} ion for each solution.

This experimental approach involves an interesting problem. The reaction which we use to prepare FeNCS^{2+} ion solutions, shown in Equation 5, is reversible, so it does not proceed to completion. How, then, can we prepare solutions with known FeNCS^{2+} ion concentrations?

To prepare a solution of known FeNCS^{2+} ion concentration, we exploit the equilibrium constant expression for the reaction. If we create an equilibrium mixture in which the Fe^{3+} ion concentration is relatively high, the equilibrium constant expression indicates that the SCN^- ion concentration for this mixture will be relatively low. Thus, by preparing a solution in which the initial Fe^{3+} ion concentration is much higher than that of SCN^- ion, we can force the reaction to proceed nearly to completion. At equilibrium, the SCN^- ion concentration will drop almost to zero. This situation is similar to a limiting reagent problem, in that the equilibrium FeNCS^{2+} ion concentration approximates the initial SCN^- ion concentration. We may use this approximation to calculate the FeNCS^{2+}

ion concentration of each of the solutions we use to prepare our Beer's Law plot.

Determining K_{eq} for the Formation of FeNCS^{2+} Ion

To determine K_{eq} for formation of FeNCS^{2+} ion, we will prepare five reaction mixtures in which we vary the SCN^- ion concentration while keeping the Fe^{3+} ion concentration constant. These mixtures will have Fe^{3+} and SCN^- ion concentrations of similar magnitude, unlike the mixtures we use to prepare the Beer's Law plot. We will measure the % T of each equilibrium mixture at 447 nm. Using Equation 7, we will convert each % T to its equivalent absorbance. We will determine the equilibrium FeNCS^{2+} ion concentration for each mixture, using the calculated absorbances and the Beer's Law plot. Finally, we will calculate the equilibrium Fe^{3+} and SCN^- ion concentrations for each mixture by subtracting the equilibrium FeNCS^{2+} ion concentration from the initial concentrations of these ions.

To illustrate this approach, suppose we make an equilibrium mixture by combining 5.00 mL of $2.00 \times 10^{-3} \text{M Fe(NO}_3)_3$ in 0.10M HNO_3 solution, 2.50 mL of $2.00 \times 10^{-3} \text{M NaSCN}$ in 0.10M HNO_3 solution, and 2.50 mL of 0.10M HNO_3 solution. After mixing, we find the % T of the solution at 447 nm to be 47.6%. To determine the equilibrium FeNCS^{2+} ion concentration, we first express % T as the equivalent absorbance, using Equation 7.

$$\begin{aligned} A &= 2.000 - \log 47.6 \\ &= 2.000 - 1.678 = 0.322 \end{aligned}$$

From a previously prepared Beer's Law plot, we determine the FeNCS^{2+} ion concentration that corresponds to this absorbance. Let us say that this concentration is $1.44 \times 10^{-4} \text{M}$.

We can calculate the initial Fe^{3+} ion concentration in the mixture from the volume and concentration of $\text{Fe(NO}_3)_3$ solution added and the volume of the final equilibrium mixture, using Equation 8.

$$\begin{aligned} \text{initial Fe}^{3+} \text{ ion concentration} &= \frac{\left(\begin{array}{l} \text{volume of} \\ \text{Fe(NO}_3)_3 \text{ stock} \\ \text{solution, mL} \end{array} \right) \left(\begin{array}{l} \text{concentration of} \\ \text{Fe(NO}_3)_3 \text{ stock} \\ \text{solution, mol L}^{-1} \end{array} \right)}{\text{volume of equilibrium mixture, mL}} \\ &= \frac{(5.00 \text{ mL})(2.00 \times 10^{-3} \text{ M})}{10.00 \text{ mL}} \\ &= 1.00 \times 10^{-3} \text{ M} \end{aligned} \quad (\text{Eq. 8})$$

Because some of the Fe^{3+} ion initially present is consumed through FeNCS^{2+} ion formation, we can calculate the equilibrium Fe^{3+} ion concentration by subtracting the equilibrium FeNCS^{2+} ion concentration from the initial Fe^{3+} ion concentration. This relationship is expressed in Equation 9.

$$\begin{aligned} \text{equilibrium } \text{Fe}^{3+} \text{ ion concentration, mol}^{-1} &= \\ \left(\begin{array}{c} \text{initial } \text{Fe}^{3+} \text{ ion} \\ \text{concentration,} \\ \text{mol L}^{-1} \end{array} \right) &- \left(\begin{array}{c} \text{equilibrium} \\ \text{FeNCS}^{2+} \text{ ion} \\ \text{concentration, mol L}^{-1} \end{array} \right) & \text{(Eq. 9)} \\ &= (1.00 \times 10^{-3} M) - (1.44 \times 10^{-4} M) \\ &= 8.56 \times 10^{-4} M \end{aligned}$$

Note that we can directly subtract concentrations because the total volumes of the initial and equilibrium solutions are identical. Using similar reasoning and Equations 10 and 11, we can calculate the equilibrium SCN^- ion concentration to be $3.56 \times 10^{-4} M$.

$$\begin{aligned} \text{initial } \text{SCN}^- \text{ ion concentration, mol L}^{-1} &= \\ \frac{\left(\begin{array}{c} \text{volume of} \\ \text{NaSCN stock} \\ \text{solution, mL} \end{array} \right) \left(\begin{array}{c} \text{concentration of} \\ \text{NaSCN stock solution,} \\ \text{mol L}^{-1} \end{array} \right)}{\text{volume of equilibrium mixture, mL}} & \text{(Eq. 10)} \\ &= \frac{(2.50 \text{ mL})(2.00 \times 10^{-3} \text{ mol L}^{-1})}{10.00 \text{ mL}} \\ &= 5.00 \times 10^{-4} M \end{aligned}$$

$$\begin{aligned} \text{equilibrium } \text{SCN}^- \text{ ion concentration, mol L}^{-1} &= \\ \left(\begin{array}{c} \text{initial } \text{SCN}^- \text{ ion} \\ \text{concentration,} \\ \text{mol L}^{-1} \end{array} \right) &- \left(\begin{array}{c} \text{equilibrium, FeNCS}^{2+} \\ \text{ion concentration,} \\ \text{mol L}^{-1} \end{array} \right) & \text{(Eq. 11)} \\ &= (5.00 \times 10^{-4} M) - (1.44 \times 10^{-4} M) \\ &= 3.56 \times 10^{-4} M \end{aligned}$$

We can now write an equilibrium constant expression for the formation of FeNCS^{2+} ion, based on the general expression shown in Equation 4. Substituting the calculated FeNCS^{2+} , Fe^{3+} , and SCN^- ion concentrations into this expression, we find that, for the solution under discussion, K_{eq} is 4.7×10^2 . Remember that K_{eq} is dependent on reaction temperature.

In this experiment you will prepare six standard solutions and five equilibrium mixtures of FeNCS^{2+} ion, each with a different initial SCN^- concentration. You will determine %T for each of the standard solutions, and prepare a Beer's Law plot. Using data from the equilibrium mixtures, you will write an equilibrium constant expression for the reaction. Based on this expression, you will determine and compare K_{eq} for each mixture, and

determine a mean K_{eq} for this reaction at the reaction temperature.

Procedure

Chemical Alert

6M ammonia solution—toxic, corrosive, and irritant
aqueous nitric acid solutions—highly toxic and strong oxidant
iron(III) nitrate in nitric acid solutions—toxic, irritant, and oxidant
sodium thiocyanate in nitric acid solutions—toxic, corrosive, irritant, and oxidant
iron(III) nitrate in sodium thiocyanate-nitric acid solutions—toxic, irritant, and oxidant

Caution: Wear departmentally approved eye protection while doing this experiment.

I. Preparing Standard Solutions for the Beer's Law Plot

1. Label six 50.00-mL volumetric flasks "S1" through "S6."

Caution: The solutions mixed with nitric acid in this experiment are toxic, irritating, and oxidant. Contact with skin can cause severe burns and skin discoloration. Sodium thiocyanate in nitric acid solution is also corrosive. Avoid inhaling the vapors and ingesting these solutions. If you spill any solution, immediately notify your laboratory instructor. Immediately wash affected areas of your skin and clothing.

Note: Your laboratory instructor will demonstrate and describe the proper use of a volumetric pipet for accurate solution measurement. **Never** use mouth suction to draw liquids into a pipet.

2. Pipet 10.00 mL of $2.00 \times 10^{-1} M \text{Fe}(\text{NO}_3)_3$ solution into each of the volumetric flasks, as indicated in Table 1. Pipet 1.00, 2.00, 3.00, 4.00, and 5.00 mL of $2.00 \times 10^{-3} M \text{NaSCN}$ solution into flasks S2 through S6, respectively (none in flask S1). Record the $\text{Fe}(\text{NO}_3)_3$ and NaSCN solution concentrations from the reagent

Table 1 Standard solutions for FeNCS^{2+} ion Beer's Law plot

solution	$2.00 \times 10^{-1} M$ $\text{Fe}(\text{NO}_3)_3$ in $0.10 M \text{HNO}_3$, mL	$2.00 \times 10^{-3} M$ NaSCN in $0.10 M \text{HNO}_3$, mL	total volume of solution, mL (including additional HNO_3)
S1 (blank)	10.00	0.00	50.00
S2	10.00	1.00	50.00
S3	10.00	2.00	50.00
S4	10.00	3.00	50.00
S5	10.00	4.00	50.00
S6	10.00	5.00	50.00

bottles on Data Sheet 1. Record the volume of NaSCN solution added to flasks S2–S6 on Data Sheet 1.

3. Add $0.10 M$ nitric acid solution to each volumetric flask until the bottom of the meniscus is even with the etched mark on the flask neck. Stopper the flasks. While holding the stopper firmly in place, invert each flask several times to thoroughly mix the solution.

II. Spectrophotometrically Analyzing the Standard Solutions

Note: Your laboratory instructor will demonstrate the use of the spectrophotometers in your laboratory and methods for cleaning and filling cuvettes.

4. Set the wavelength of the spectrophotometer to 447 nm. Adjust the % T reading on the spectrophotometer to zero.

5. Obtain two cuvettes. Rinse one cuvette with solution S1, discarding the rinse in a 600-mL beaker that you labeled "Discarded Equilibrium Mixtures."

Fill the rinsed cuvette with solution S1. This solution will serve as a "blank," or reference solution. Insert the cuvette into the sample holder so that the guideline on the cuvette is lined up with the mark on the sample holder. Close the sample holder cover and adjust the light control knob until the meter reads 100% T (zero absorbance). Save the reference cuvette filled with solution S1 for periodic calibration checks.

6. Rinse the second cuvette with solution S2, discarding the rinse in the "Discarded Equilibrium Mixtures" beaker. Fill the cuvette with solution S2, and insert it into the sample holder. Close the sample holder cover. Read the % T of solution S2. Record this % T on

Data Sheet 1. Discard the solution in the cuvette into the "Discarded Equilibrium Mixtures" beaker.

7. Repeat Step 6 using the remaining solutions, S3 through S6. Record the % T for each of these solutions on Data Sheet 1.

8. After your laboratory instructor has checked your data, discard all solutions from the flasks into the "Discarded Equilibrium Mixtures" beaker.

9. Wash the cuvettes and volumetric flasks with soap or detergent solution. Rinse them three times with tap water and once with distilled or deionized water. Allow the cuvettes and volumetric flasks to drain.

III. Preparing and Analyzing the Equilibrium Mixtures

10. Obtain six clean, dry 18×150 -mm test tubes, and label them E1–E6.

11. Pipet 5.00 mL of $2.00 \times 10^{-3} M \text{Fe}(\text{NO}_3)_3$ solution into each of the clean, dry, labeled test tubes. Pipet the volumes of $2.00 \times 10^{-3} M \text{NaSCN}$ listed in Table 2 into each of the test tubes.

Calculate the amount of $1.0 \times 10^{-1} M \text{HNO}_3$ solution that you must add to each test tube so that the total solution volume is 10 mL. Pipet the required amounts of $1.0 \times 10^{-1} M \text{HNO}_3$ into each test tube. Thoroughly mix the solutions in the test tubes by tightly covering the test tubes with parafilm and inverting them several times.

Record the $\text{Fe}(\text{NO}_3)_3$ and NaSCN concentrations from the reagent bottles on Data Sheet 2. Record the volumes of reagents used for solutions E2–E6 on Data Sheet 2.

12. Rinse a cuvette with solution E1. Discard the rinse into the "Discarded Equilibrium Mixtures" beaker. Fill the cuvette with solution E1. Use solution E1 as a blank

Table 2 Equilibrium mixtures for FeNCS^{2+} ion study

solution	$2.00 \times 10^{-3} \text{M}$ $\text{Fe}(\text{NO}_3)_3$ in 0.10M HNO_3 , mL	$2.00 \times 10^{-3} \text{M}$ NaSCN in 0.10M HNO_3 , mL	total volume of solution, mL (including additional HNO_3)
E1 (blank)	5.00	0.00	10.00
E2	5.00	1.00	10.00
E3	5.00	2.00	10.00
E4	5.00	3.00	10.00
E5	5.00	4.00	10.00
E6	5.00	5.00	10.00

to adjust the spectrophotometer to zero absorbance, following the instructions in Step 5.

13. Rinse the second cuvette with solution E2. Discard the rinse into the "Discarded Equilibrium Mixtures" beaker. Fill the cuvette with solution E2, and read the %T. Record the %T of solution E2 on Data Sheet 2.

14. Repeat Step 13 using solutions E3–E6.

15. Obtain a thermometer. Measure the temperature of each equilibrium mixture, rinsing and drying the thermometer after each temperature measurement. Record these temperatures on Data Sheet 2.

16. After your laboratory instructor has checked your data and initialled your notebook, discard all solutions into the "Discarded Equilibrium Mixtures" beaker.

Note: Do Part IV if your laboratory instructor so directs you. If you are not directed to do Part IV, dispose of the "Discarded Equilibrium Mixtures" beaker contents into a disposal container as directed by your laboratory instructor.

The following will be performed by the stockroom. Please put waste in the appropriately labeled container.

IV. Treating the "Discarded Equilibrium Mixtures" for Disposal

Caution: 6M ammonia solution is toxic, corrosive, and irritating. Prevent eye, skin, and clothing contact. Permanent fogging of soft contact lenses may result from NH_3 vapors. Avoid inhaling vapors and ingesting the solution. If you spill any NH_3 solution, immediately notify your laboratory instructor.

17. Carefully add 6M NH_3 solution to the "Discarded Equilibrium Mixtures" beaker until the solution pH is 6.

18. If a precipitate should form, filter the solution. Transfer the precipitate into the container provided by your laboratory instructor.

19. Pour the filtrate or the solution into the drain, diluting with a large amount of running water.

20. Wash the beaker, test tubes, and cuvettes with soap or detergent solution. Rinse three times with tap water and once with distilled water. Allow the beaker, test tubes, and cuvettes to drain.

Caution: Wash your hands thoroughly with soap or detergent before leaving the laboratory.

Calculations

Do the following calculations and record the results on the appropriate sections of your Data Sheets.

II. Spectrophotometrically Analyzing the Standard Solutions

1. Calculate the initial molar SCN^- ion concentrations for the six standard solutions, using Equation 10. Assume that NaSCN is completely dissociated, that is, $[\text{SCN}^-] = [\text{NaSCN}]$.

2. Calculate the equilibrium molar FeNCS^{2+} ion concentrations for the standard solutions. Assume all SCN^- ions are complexed with Fe^{3+} ion to form FeNCS^{2+} ion and that $[\text{FeNCS}^{2+}] = [\text{SCN}^-]$.

3. Calculate the equivalent absorbances for the %T readings at 447 nm, using Equation 7.

4. Prepare a Beer's Law plot for the FeNCS^{2+} ion standard solutions, using the graph paper later in this experiment. Plot equivalent absorbance (A) at 447 nm on the ordinate and molar FeNCS^{2+} ion concentration on the abscissa. Draw the best straight line through your data points and the origin. Make sure your laboratory instructor approves your plot and initials your data sheet.

III. Preparing and Analyzing the Equilibrium Mixtures

5. Calculate the initial Fe^{3+} and SCN^- ion concentrations for solutions E2–E6, using Equations 8 and 10.

6. Calculate the equivalent absorbances for the % T readings at 447 nm, using Equation 7.

7. For each equilibrium solution, determine the FeNCS^{2+} ion concentration from your Beer's Law plot. Record these concentrations on Data Sheet 2.

8. Calculate the equilibrium Fe^{3+} and SCN^- ion concentrations, using Equations 9 and 11.

9. Write the equilibrium constant expression for the formation of FeNCS^{2+} ion, based on the stoichiometric relationship in Equation 5.

10. Calculate K_{eq} for solutions E2–E6, using the equilibrium concentrations determined in Calculations 7 and 8.

11. Calculate the mean K_{eq} for the formation of FeNCS^{2+} ion.