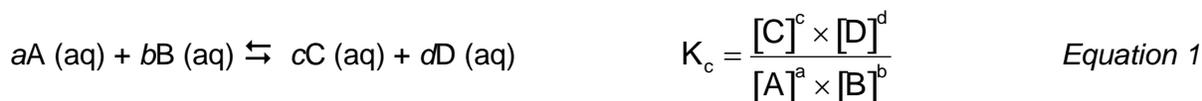# Determination of K_c for a Complex Ion Formation

Objectives

- Find the value of the equilibrium constant for formation of $FeSCN^{2+}$ by using the visible light absorption of the complex ion.
- Confirm the stoichiometry of the reaction.

Background

In the study of chemical reactions, chemistry students first study reactions that go to completion. Inherent in these familiar problems—such as calculation of theoretical yield, limiting reactant, and percent yield—is the assumption that the reaction can consume *all* of one or more reactants to produce products. In fact, most reactions do not behave this way. Instead, reactions reach a state where, after mixing the reactants, a stable mixture of reactants and products is produced. This mixture is called the *equilibrium state*; at this point, chemical reaction occurs in both directions at equal rates. Therefore, once the equilibrium state has been reached, no further change occurs in the concentrations of reactants and products.
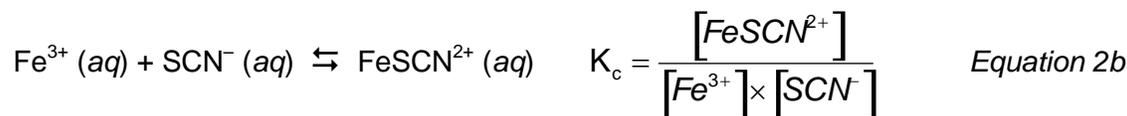
The equilibrium constant, K, is used to quantify the equilibrium state. The expression for the equilibrium constant for a reaction is determined by examining the balanced chemical equation. For a reaction involving aqueous reactants and products, the equilibrium constant is expressed as a ratio between reactant and product concentrations, where each term is raised to the power of its reaction coefficient (*Equation 1*). When an equilibrium constant is expressed in terms of molar concentrations, the equilibrium constant is referred to as K_c. The value of this constant at equilibrium is always the same, regardless of the initial reaction concentrations. At a given temperature, whether the reactants are mixed in their exact stoichiometric ratios or one reactant is initially present in large excess, the ratio described by the equilibrium constant expression will be achieved once the reaction composition stops changing.

$$aA \text{ (aq)} + bB \text{ (aq)} \rightleftharpoons cC \text{ (aq)} + dD \text{ (aq)} \qquad K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} \qquad \textit{Equation 1}$$

We will be studying the reaction that forms the reddish-orange iron (III) thiocyanate complex ion, $Fe(H_2O)_5SCN^{2+}$ (*Equation 2a*). The actual reaction involves the displacement of a water ligand by thiocyanate ligand, SCN^-.

$$Fe(H_2O)_6^{3+} \text{ (}aq\text{)} + SCN^- \text{ (}aq\text{)} \rightleftharpoons Fe(H_2O)_5SCN^{2+} \text{ (}aq\text{)} + H_2O \text{ (}l\text{)} \qquad \textit{Equation 2a}$$

For simplicity, and because water ligands do not change the net charge of the species, water can be omitted from the formulas of $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5SCN^{2+}$; thus $Fe(H_2O)_6^{3+}$ is usually written as Fe^{3+} and $Fe(H_2O)_5SCN^{2+}$ is written as $FeSCN^{2+}$ (*Equation 2b*). Also, because the concentration of liquid water is essentially unchanged in an aqueous solution, we can write a simpler expression for K_c that expresses the equilibrium condition only in terms of species with variable concentrations.

$$Fe^{3+}\ (aq) + SCN^-\ (aq) \leftrightharpoons FeSCN^{2+}\ (aq) \qquad K_c = \frac{\left[FeSCN^{2+}\right]}{\left[Fe^{3+}\right] \times \left[SCN^-\right]} \qquad \text{\textit{Equation 2b}}$$

In this experiment, students will create several different aqueous mixtures of Fe^{3+} and SCN^-. Since this reaction reaches equilibrium nearly instantly, these mixtures turn reddish-orange very quickly due to the formation of the product $FeSCN^{2+}$ (aq). The intensity of the color of the mixtures is proportional to the concentration of product formed at equilibrium. As long as all mixtures are measured at the same temperature, the ratio described in *Equation 2b* will be the same.

Measurement of [FeSCN^{2+}]. Since the complex ion product is the only strongly colored species in the system, its concentration can be determined by measuring the intensity of the orange color in equilibrium systems of these ions. Two methods (visual inspection and spectrophotometry) can be employed to measure the equilibrium molar concentration of $FeSCN^{2+}$, as described in the *Procedure* section. Your instructor will tell you which method to use. Both methods rely on Beer's Law (*Equation 3*). The absorbance, *A*, is directly proportional to two parameters: *c* (the compound's molar concentration) and path length, ℓ (the length of the sample through which the light travels). Molar absorptivity ε, is a constant that expresses the absorbing ability of a chemical species at a certain wavelength. The absorbance, *A*, is roughly correlated with the color intensity observed visually; the more intense the color, the larger the absorbance.

$$A = \varepsilon \ell c \qquad\qquad \text{\textit{Equation 3}}$$

In the visual inspection method, you will match the color of two solutions with different concentrations of $FeSCN^{2+}$ by changing the depth of the solutions in a vial. As pictured in Figure 1, the solution on the left is more concentrated than the one on the right. However, when viewed from directly above, their colors can be made to "match" by decreasing the depth of the more concentrated solution. When the colors appear the same from above, the absorbances, *A*, for each solution are the same; however, their concentrations and path lengths are not.
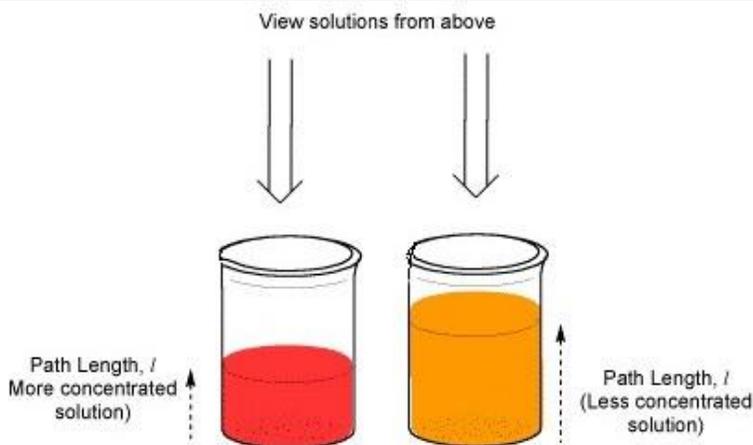

Figure 1: Solution depths (path lengths) of two samples containing different concentrations of $FeSCN^{2+}$ can be adjusted so that their apparent color looks the same when viewed from above.

If a standard sample with known concentration of $FeSCN^{2+}$ is created, measurement of the two path lengths for the "matched" solutions allows for calculation of the molar concentration of $FeSCN^{2+}$ in any mixture containing that species (*Equation 4*). This equation is an application of Beer's Law, where A/ε for matched samples are equal. Therefore, the product of the path length, ℓ, and molar concentration, c, for each sample are equal.

$$\ell_1 \times c_1 = \ell_2 \times c_2 \qquad\qquad\qquad \textit{Equation 4}$$

By using a spectrophotometer, the absorbance, A, of a solution can also be measured directly. Solutions containing $FeSCN^{2+}$ are placed into the spectrophotometer and their absorbances at 447 nm are measured. In this method, the path length, ℓ, is the same for all measurements. Rearrangement of *Equation 3* allows for calculation of the molar concentration, c, from the known value of the constant $\varepsilon \times \ell$. The value of this constant is determined by plotting the absorbances, A, vs. molar concentrations, c, for several solutions with known concentration of $FeSCN^{2+}$ (*Figure 2*). The slope of this calibration curve is then used to find unknown concentrations of $FeSCN^{2+}$ from their measured absorbances.
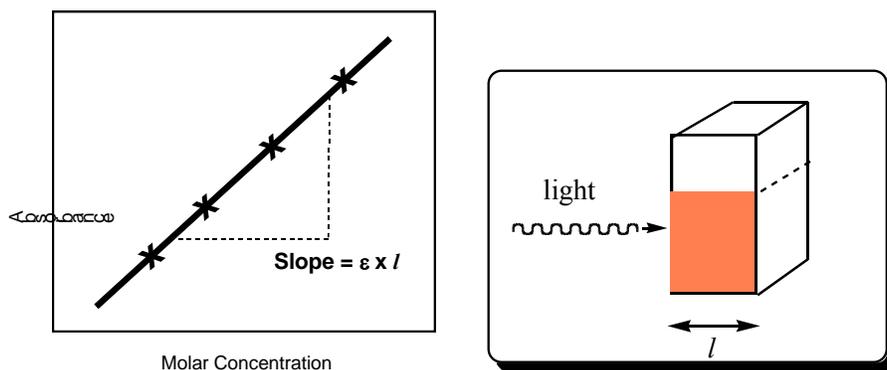

Figure 2: Plots of *A* vs. *c* for solutions with known [$FeSCN^{2+}$] can be used as a *calibration curve*. This plot is used to determine [$FeSCN^{2+}$] in solutions where that value is not known. The path length, *l*, is demonstrated in the diagram of a cuvet.

Calculations. In order to determine the value of K_c, the equilibrium values of [Fe^{3+}], [SCN^-], and [$FeSCN^{2+}$] must be known. The equilibrium value of [$FeSCN^{2+}$] was determined by one of the two methods described previously; its initial value was zero, since no $FeSCN^{2+}$ was added to the solution.

The equilibrium values of [Fe^{3+}] and [SCN^-] can be determined from a reaction table (*'ICE'* table) as shown in *Table 1*. The initial concentrations of the reactants—that is, [Fe^{3+}] and [SCN^-] prior to any reaction—can be found by a dilution calculation based on the values from *Table 2* found in the procedure. Once the reaction reaches equilibrium, we assume that the reaction has shifted forward by an amount, *x*. The equilibrium concentrations of the reactants, Fe^{3+} and SCN^-, are found by subtracting the equilibrium [$FeSCN^{2+}$] from the initial values. Once all the equilibrium values are known, they can be applied to *Equation 2b* to determine the value of K_c.

Table 1: Reaction ICE Table

	Fe^{3+}	$+$ SCN^-	$\leftrightarrows$ $FeSCN^{2+}$
*I*nitial Concentration	$[Fe^{3+}]_i$	$[SCN^-]_i$	0
*C*hange in Concentration	$- x$	$- x$	$+ x$
*E*quilibrium Concentration	$[Fe^{3+}]_i - x$	$[SCN^-]_i - x$	$x = [FeSCN^{2+}]$

The reaction "ICE" table demonstrates the method used in order to find the equilibrium concentrations of each species. The values that come directly from the experimental procedure are found in the shaded regions. From these values, the remainder of the table can be completed.

Standard Solutions of $FeSCN^{2+}$. In order to find the equilibrium $[FeSCN^{2+}]$, both methods require the preparation of standard solutions with known $[FeSCN^{2+}]$. These are prepared by mixing a small amount of dilute KSCN solution with a more concentrated solution of $Fe(NO_3)_3$. The solution has an overwhelming excess of Fe^{3+}, driving the equilibrium position far towards products. As a result, the equilibrium $[Fe^{3+}]$ is very high due to its large excess, and therefore the equilibrium $[SCN^-]$ must be very small. In other words, we can assume that ~100% of the SCN^- is reacted meaning that SCN^- is a limiting reactant resulting in the production of an equal amount of $FeSCN^{2+}$ product. Examine the K_c-expression to prove this to yourself. In summary, due to the large excess of Fe^{3+}, the equilibrium concentration of $FeSCN^{2+}$ can be approximated as the initial concentration of SCN^-.

Procedure

Safety: The iron(III) nitrate solutions contain nitric acid. Avoid contact with skin and eyes; wash hands frequently during the lab and wash hands and all glassware thoroughly after the experiment. Collect all your solutions during the lab and dispose of them in the proper waste container.

Materials and Equipment

Solutions: Iron(III) nitrate (2.00×10^{-3} M) in 1 M HNO_3; Iron(III) nitrate (0.200 M) in 1 M HNO_3; Potassium thiocyanate (2.00×10^{-3} M).

Materials:

Procedure C. Test tubes (large and medium size), stirring rod, 5-mL volumetric pipet*, 10-mL graduated pipet*, flat-bottomed glass vials (6), Pasteur pipets, ruler

Procedure D. Test tubes (large and medium size), stirring rod, 5-mL volumetric pipet*, 10-mL graduated pipet*, Pasteur pipets, ruler, spectrometers and cuvets* (2).

*must obtain from stockroom

A. Solution Preparation

Label two clean, dry 50-mL beakers, and pour 30-40 mL of 2.00×10^{-3} M $Fe(NO_3)_3$ (already dissolved by the stockroom in 1 M HNO_3) into one beaker. Then pour 25-30 mL of 2.00×10^{-3} M KSCN into the other beaker. At your work area, label five clean and dry medium test tubes to be used for the five test mixtures you will make. Using your volumetric pipet, add 5.00 mL of your 2.00×10^{-3} M $Fe(NO_3)_3$ solution into each of the five test tubes. Next, using your graduated pipet, add the correct amount of KSCN solution to each of the labeled test tubes, according to the table below. Rinse out your graduated pipet with deionized water, and then use it to add the appropriate amount of deionized water into each of the labeled test tubes. Stir each solution thoroughly with your stirring rod until a uniform orange color is obtained. To avoid contaminating the solutions, rinse and dry your stirring rod after stirring each solution

Table 2: Test mixtures

Mixture	Fe(NO₃)₃ solution	KSCN solution	water
1	5.00 mL	5.00 mL	0 mL
2	5.00 mL	4.00 mL	1.00 mL
3	5.00 mL	3.00 mL	2.00 mL
4	5.00 mL	2.00 mL	3.00 mL
5	5.00 mL	1.00 mL	4.00 mL

Five solutions will be prepared from 2.00×10^{-3} M KSCN and 2.00×10^{-3} M $Fe(NO_3)_3$ according to this table. Note that the total volume for each mixture is 10.00 mL, assuming volumes are additive. If the mixtures are prepared properly, the solutions will gradually become lighter in color from the first to the fifth mixture. Use this table to perform dilution calculations to find the initial reactant concentrations to use in *Figure 3*.

B. Preparation of a Standard Solution of FeSCN²⁺

Before examining the five test mixtures, prepare a standard solution with known concentration of $FeSCN^{2+}$. Obtain 15 mL of **0.200 M** $FeNO_3$. (Note the different concentration of this solution.) Rinse your volumetric pipet with a few mL of this solution, and add 10.00 mL of this solution into a clean and dry large test tube. Using your graduated pipet, add 8.00 mL deionized water to the large test tube. Rinse your graduated pipet with a few mL of 2.00×10^{-3} M KSCN. Then add 2.00 mL of the KSCN solution to the large test tube. Mix the solution with a clean and dry stirring rod until a uniform dark-orange solution is obtained. This solution should be darker than any of the other five solutions prepared previously.

C. Determination of [FeSCN²⁺] by visual inspection

Note: *Skip to part D if your instructor asks you determine [FeSCN²⁺] spectrophotometrically.*

Label five flat-bottomed vials to be used for each of the five test mixtures prepared earlier. Using a clean and dry Pasteur (dropping) pipet, transfer each solution into the properly labeled vial. Rinse the dropping pipet between solutions with a small portion of the next solution to be added. The volume of the solution transferred to the vials is not important; you will obtain the best results by nearly filling each of the vials. Label a sixth vial to be used for the standard solution.

Rinse your dropping pipet with a small portion of the standard solution. Then add the standard solution to the sixth labeled vial until it is about one-third full. Place this vial next to the vial

containing mixture 1. Using your dropping pipet, add or subtract solution from the ***standard vial*** until the color intensities observed from above exactly match. Use a white piece of paper as background when observing the colors. To avoid interference from shadows, lift the vials above the paper by several inches. Once the colors are matched, measure (to the nearest 0.2 mm) the depth of each solution with your ruler. Measure to the *bottom* of the meniscus.

Repeat the comparison and depth measurement with the remaining test mixtures (mixtures 2-5). It is likely that you will need to remove some standard solution each time you compare a new solution.

D. Spectrophotometric Determination of [FeSCN^{2+}] (optional alternative to procedure C.)
Your instructor may ask you to measure the absorbance of each test mixture using a spectrophotometer, rather than by matching the colors with a standard solution. In this case, you will be create a calibration curve that plots the absorbance of FeSCN^{2+} at 447 nm vs. molar concentration.   From this curve, you can determine [FeSCN^{2+}] in each mixture from the absorbance at 447 nm.

A few dilutions of the standard solution prepared in Part B will be used to prepare four standard solutions for your calibration curve. In addition, one 'blank' solution containing only Fe(NO$_3$)$_3$ will be used to zero the spectrophotometer. The instructor will decide if each group of students will work alone or with other groups to prepare the standards. *Figure 5* shows the preparation method for each of the standards.

Table 3: Standard Solutions for Calibration Curve

Tube	Composition
Blank	0.200 M Fe(NO$_3$)$_3$ in 1 M HNO$_3$
1	Stock Solution (Part B)
2	4.00 mL Stock + 1.00 mL H$_2$O
3	4.00 mL Stock + 2.00 mL H$_2$O
4	4.00 mL Stock + 3.00 mL H$_2$O

Four standard solutions and one blank solution will be prepared for the calibration curve. Your instructor will tell you if you need to create all these solutions or if groups can share solutions.

Fill a cuvet with the blank solution and carefully wipe off the outside with a tissue. Insert the cuvet and make sure it is oriented correctly by aligning the mark on cuvet towards the front. Close the lid. Your instructor will show you how to zero the spectrophotometer with this solution. Set aside this solution for later disposal. For each standard solution in *Figure 5*, rinse your cuvet three times with a small amount (~0.5 mL) of the standard solution to be measured, disposing the rinse solution each time. Then fill the cuvet with the standard, insert the cuvet as before and record the absorbance reading.   Finally, repeat this same procedure with five mixtures with unknown [FeSCN^{2+}] prepared in Part A, *Figure 4*. The [FeSCN^{2+}] in this solutions will be read from the calibration curve.

Name: _____   Course Section: _____
                                                    Instructor: _____

Lab Report: Determination of K_c for a Complex Ion Formation

Experimental Data

Initial Concentrations of Fe^{3+} and SCN^- in Unknown Mixtures (Part A)

Tube	Reagent Volumes (mL)			Initial Concentrations (M)	
	2.00×10^{-3} M $Fe(NO_3)_3$	2.00×10^{-3} M KSCN	Water	Fe^{3+}	SCN^-
1	5.00	5.00	0		
2	5.00	4.00	1.00		
3	5.00	3.00	2.00		
4	5.00	2.00	3.00		
5	5.00	1.00	4.00		

Show a sample dilution calculation for $[Fe^{3+}]_{initial}$ in Tube #1 only.

The Standard $FeSCN^{2+}$ Solution (Visual Method, Parts B and C)

10.00 mL of **0.200 M** $Fe(NO_3)_3$
2.00 mL of 0.00200 M KSCN
8.00 mL of water

Equilbrium $[FeSCN^{2+}]$ in Standard Solution: _____ M

Note that since $[Fe^{3+}]>>[SCN^-]$ in the Standard Solution, the reaction is forced to completion, thus causing <u>all</u> the SCN^- to convert to $FeSCN^{2+}$.

Show the stoichiometry and dilution calculations used to obtain this value.

Equilibrium Concentrations of FeSCN^{2+} in Mixtures (Visual Method, Part C)

Tube	Solution Depths (mm)		[FeSCN^{2+}]$_{equil}$ (M)
	Mixtures	Standard	
1			
2			
3			
4			
5			

Show a sample calculation for [FeSCN^{2+}]$_{equil}$ in Tube #1 only.

Calibration Curve Data (Spectrophotometric Method, Part D)

Tube	Absorbance	[FeSCN^{2+}] (M)
Blank		
1		
2		
3		
4		

Show a sample dilution calculation for [FeSCN^{2+}] in Tube #1 and 2 only.

*Note that since [Fe^{3+}]>>[SCN$^-$] in the Standard Solutions, the reaction is forced to completion, thus causing essentially **all** the added SCN$^-$ to be converted to FeSCN^{2+}.*

Plot Absorbance vs. [FeSCN^{2+}] for the standard solutions. Obtain an equation for the line. This can be used to determine the [FeSCN^{2+}] in the table below. Attach your plot to this report.

Linear Equation (A vs. [FeSCN^{2+}]) of Calibration Curve:

Test mixtures (Spectrophotometric Method, Part D)

Mixture	Absorbance	[FeSCN^{2+}] (M)
1		
2		
3		
4		
5		

Show a sample calculation for [FeSCN^{2+}] in mixture 1.

Calculations and Analysis

The reaction that is assumed to occur in this experiment is:

$$Fe^{3+} (aq) + SCN^{-} (aq) \leftrightarrows FeSCN^{2+} (aq)$$

- Write the equilibrium constant expression for the reaction.

- Create a **Reaction Table** (or ICE table), as in *Table 1*, to demonstrate how the values below are calculated. Use the data for Mixture #1 only. Start with the known values for the initial concentrations of each species and the final value of $[FeSCN^{2+}]$ from the data table on the previous page. Show how you find the value of the stoichiometric change in reaction concentrations that occurs, and the resulting equilibrium concentrations of the reactants.

Show a sample calculation for the value of K_c using the data for Tube #1.

Using the same method you outlined above, complete the table for all the equilibrium concentrations and value of K_c.

Tube	Equilibrium Concentrations (M)			K_c
	Fe^{3+}	SCN^-	$FeSCN^{2+}$	
1				
2				
3				
4				
5				

Average value of K_c _____

(Use reasonable number of significant digits, based on the distribution of your K_c values.)

Optional Analysis: Is an alternative reaction stoichiometry supported?

Suppose that instead of forming $FeSCN^{2+}$, the reaction between Fe^{3+} and SCN^- resulted in the formation of $Fe(SCN)_2^+$. The reaction analogous to *Equation 2b* would be:

$$Fe^{+3} (aq) + 2 \ SCN^- (aq) \rightleftharpoons Fe(SCN)_2^+ (aq)$$
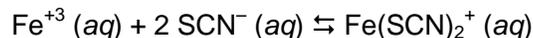
(In *Equation 2a*, that would mean two moles of SCN^- displace two moles of H_2O in $Fe(H_2O)_6^{2+}$, making $Fe(SCN)_2(H_2O)_4^+$.)

- Write the equilibrium expression for this reaction.

- Create a **Reaction Table** for Mixture #1 only (or ICE table), as in *Table 1*, to clearly show how all the values below were obtained. Then show the calculation for the value of K_c for Tube 1. Pay special attention to the stoichiometry in this system. Begin by assuming that the equilibrium value for $[Fe(SCN)_2^+]$ is be equal to ½ $[FeSCN^{+2}]$ at equilibrium obtained previously.

  (This is because the moles of SCN^- assumed to be equal to the moles of complex ion product, $FeSCN^{2+}$, in our standard solutions. In the alternate reaction, moles of product, $Fe(SCN)_2^+$, equal ½ the number of moles of SCN^- added in the standard solutions.)

- Using the method you outlined above, complete the table for all the equilibrium concentrations and values of K_c.

Tube	Equilibrium Concentrations (M)			K_c
	Fe^{3+}	SCN^-	$Fe(SCN)_2^+$	
1				
2				
3				
4				
5				

Average value of K_c _____

(Use a reasonable number of significant digits, based on the distribution of your K_c values.)

Based on the calculated values of K_c for each reaction stoichiometry, which reaction is the valid one?

_____

Briefly explain your conclusion. Compare the percent difference between the average value and the individual measurements. What does this tell you about the two possible stoichiometries? Do these reactions give consistent values of K_c for different initial reaction conditions?