Lab Investigation 5 - What Is the Formation Constant for $FeSCN^{2+}$?

GUIDING QUESTION

What is the formation constant for the $FeSCN^{2+}$ system?

INTRODUCTION

A typical chemical equation has the following form:

$$aA + bB \rightarrow cC + dD.$$
 (1)

This form of the equation assumes that the reaction proceeds completely to products. In practice, many reactions do not proceed to completion. If we measure the concentration of a reactant, it eventually reaches a value that does not change further over time. If we measure the concentration of a product, it reaches a constant value short of that predicted by the theoretical yield calculation. In these cases, we say that the reaction has reached **equilibrium**. We write the chemical reaction using equilibrium arrows instead of a single arrow:

$$aA + bB \rightleftharpoons cC + dD. \tag{2}$$

At equilibrium, the rates of the forward and reverse reactions are equal and, unless equilibrium is disturbed (stressed), no changes in reactant or product concentrations will be measured. The equilibrium arrows, one of which points in each direction, reinforce this idea.

At equilibrium, the molar concentrations of products and reactants will be fixed in a given ratio. This ratio is the equilibrium constant, K_{eq} , which is determined by substituting molar concentrations (indicated by the square brackets) into the equilibrium constant equation. The general form of this equation is:

$$K_{\rm eq} = \frac{[\mathbf{C}]^{\rm c}[\mathbf{D}]^{\rm d}}{[\mathbf{A}]^{\rm a}[\mathbf{B}]^{\rm b}}.$$
(3)

Reactants mixed in arbitrary concentrations will react until the ratio of the concentrations reaches the value of the equilibrium constant according to equation 3. The value of K_{eq} varies with temperature; therefore, the temperature at which the equilibrium constant was determined must be referenced.

In this laboratory experiment, a combination of solution chemistry, stoichiometry and spectrophotometric analysis will be used to determine the equilibrium constant for a reaction between iron(III) ion (Fe^{3+}) and thiocyanate ion (SCN⁻). In acidic solution, these ions form a blood-red complex ion as shown in equation 4:

$$\operatorname{Fe}^{3+}(aq) + \operatorname{SCN}^{-}(aq) \rightleftharpoons \operatorname{FeSCN}^{2+}(aq).$$
 (4)

The equilibrium constant for equation 4 can be expressed using the concentrations of the three components:

$$K = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^{-}]}.$$
(5)

In order to calculate the equilibrium constant, one must simultaneously determine the concentrations of all three of the components. In this experiment, you will measure the concentration of FeSCN²⁺ at equilibrium by measuring its absorbance at 470 nm. Since Fe³⁺ and SCN⁻ do not absorb light at this wavelength, they do not interfere with the measurements. If you know the initial (before equilibrium) concentrations of Fe³⁺ and SCN⁻, you can use a reaction table to calculate the equilibrium concentrations of these two ions at equilibrium.

For example, you might initially mix equal volumes of 2.0 M Fe³⁺ and 2.0 M SCN⁻. The term "initial concentration" can be confusing. Even though the reaction appears to go instantaneously upon mixing the reactants, the "initial concentrations" in the reaction table are those after dilution has been taken into consideration but before any reaction occurs. Thus, the initial line in the reaction table for mixing equal volumes of 2.0 M Fe³⁺ and 2.0 M SCN⁻ should have entries of 1.0 M under Fe³⁺ and SCN⁻ due to dilution. The initial concentration of FeSCN²⁺ is 0.0 M. In our example, you might measure an equilibrium (final) concentration of 0.6 M FeSCN²⁺. With the final concentration of the product, you can determine the change in product concentration and, therefore, the changes in the reactant concentrations. The reaction table is shown below.

	Fe ³⁺	+	SCN ¹⁻	≠	FeSCN ²⁺
initial	1.0 <i>M</i>		1.0 <i>M</i>		0.0 <i>M</i>
Δ	– 0.6 <i>M</i>		– 0.6 <i>M</i>		+ 0.6 <i>M</i>
equilibrium (final)	0.4 <i>M</i>		0.4 <i>M</i>		0.6 <i>M</i>

In this experiment, 0.2 M HNO₃ serves as the solvent. The acid adds a large (compared to the reactants) amount of H⁺. This prevents side reactions such as the formation of FeOH²⁺, a brownish species that can affect the results. The acid concentration is high enough that it is not affected by the reaction and remains constant at 0.2 M.

You will prepare six standard solutions of FeSCN^{2+} to calibrate a spectrophotometer. A fair question is "How do I know the concentration of FeSCN^{2+} in my standard solutions if it is in equilibrium with Fe^{3+} and SCN^{-} ?" In the standard solutions, the concentration of Fe^{3+} is much higher than that of SCN^{-} . This forces the equilibrium as far to the right (toward FeSCN^{2+}) as possible. Therefore, the concentration of FeSCN^{2+} in a standard solution will be very nearly equal to the initial concentration of SCN^{-} used in preparing it. The absorbance measurement at

470 nm will correlate to the concentration of complex ion, and an accurate calibration curve (Beer's law plot) can be obtained. Recall that the calibration curve gives you a relationship between the concentration of a species in solution and its absorbance at a given wavelength: $(A = \epsilon lc)$. Using the linear regression of the calibration curve in Part A, you will determine the concentration of

 $FeSCN^{2+}$ ion in each of five equilibrium mixtures in Part B. An equilibrium constant can then be determined for each mixture; the average should be the equilibrium constant value for the formation of the $FeSCN^{2+}$ ion.

In Part A of this experiment, you will prepare FeSCN^{2+} solutions of known concentrations, measure their absorbances at 470 nm, and produce a calibration curve. In Part B, you will make equilibrium mixtures of Fe^{3+} , SCN^- , and FeSCN^{2+} . You will determine the concentration of FeSCN^{2+} from its absorbance at 470 nm and your calibration curve from Part A. Then, using reaction tables, you will calculate the equilibrium concentrations of Fe^{3+} and SCN^- , and determine the equilibrium constant for the formation of FeSCN^{2+} .

GOALS

As you complete this investigation you will:

- 1 Design a procedure for measuring the concentration of $FeSCN^{2+}$ from the color intensity of a solution.
- **2** Design and carry out a procedure to measure the equilibrium constant for a complex ion formation reaction.

MATERIALS AVAILABLE FOR USE

0.100 M Fe(NO₃)₃ in 0.2 M HNO₃

 $5.00\times 10^{-4}~M$ NaSCN in 0.2 $M~{\rm HNO_3}$

 $0.00200\ M\ {\rm Fe}({\rm NO}_3)_3$ in $0.2\ M\ {\rm HNO}_3$

0.00200 M NaSCN in 0.2 M HNO_3 $\,$

Pipettors and tips

Vernier LabPro system with colorimeter

Cuvettes

Kimwipes

SAFETY PRECAUTIONS

<u>CAUTION</u>: Wear goggles at all times.

<u>CAUTION</u>: Nitric acid is listed as a corrosive. Corrosives can attack the skin and cause permanent damage to the eyes. Nitric acid and iron(III) nitrate are listed as oxidants. Sodium thiocyanate is listed as toxic and an irritant. With the exception of nitric acid, the concentrations of all these materials are quite low, however. If you spill any of these chemicals on skin or clothing, flush the area immediately with water.

WASTE DISPOSAL

All of the solutions prepared in this experiment, as well as excess NaSCN solution, should be discarded in the waste container. You may wish to have a waste beaker in your work area to collect waste while you are doing the experiment. Make sure it is labeled. Always remember not to overfill the waste bottle. If your waste bottle is full, please alert your lab instructor.

PROCEDURE

Please print the worksheet for this lab. You will need this sheet to record your data.

Part A: Preparation of Standard Solutions and Beer's Law Plot

Because the $FeSCN^{2+}$ complex ion is a colored species, a device that measures light absorbance can generate data for a Beer's law calibration curve. A plot of absorbance versus concentration for a set of solutions will have a linear range that can then be used to find concentration given absorbance.

Part B: Finding the Formation Constant (K_f)

Once you have generated a calibration curve for the absorbance of the FeSCN²⁺ complex ion, mix four or five combinations of Fe³⁺ and SCN⁻. Use varying amounts of 0.00200 M KSCN and 0.00200 M Fe(NO₃)₃ for each solution and make the total volume of each solution 6.00 mL.

As a point of reference all groups should prepare one reaction mixture with 3.00 mL Fe^{3+} solution and 3.00 mL SCN^- solution with no added water.

Determine the absorbance of the $FeSCN^{2+}$ complex ion after equilibrium is established in each solution. (Equilibrium is established within a few seconds after the reactants are mixed.)

Since neither Fe^{3+} nor SCN^- is in large excess, the $[\text{FeSCN}^{2+}]_{\text{eq}}$ cannot be calculated based on initial concentrations; it must be determined using the calibration curve once the reaction is at equilibrium. Once that concentration is known, you should be able to calculate the concentrations of the other ions at equilibrium. Use the equilibrium concentrations to determine the value of K_f for this system.

There is a post-lab assignment in WebAssign that will enable you to check your calculations.

INTERACTIVE POSTER SESSION

Once your group has completed work, prepare a whiteboard that you can use to share and justify your ideas. See the handout¹ provided for details on this process.

REPORT

Once you have completed your research, you will need to prepare an *investigation report* that consists of three sections. This report may require more than 2 pages with data tables. This report must be typed and any diagrams, figures, or tables should be embedded into the document.

 $^{^{1}../\}text{poster/manual.html}$

Section 1: What concept were you investigating? Relate this concept to the guiding question. What is the formation constant for the $FeSCN^{2+}$ system? Discuss the relationship of equilibrium constant and LeChatelier's principle to the guiding question.

Section 2: How did you go about your work and why did you conduct your investigation in this way? It is important that you explain the importance of the concentration of the reactants in creating the calibration curve.

Section 3: What is your argument? Report an average $K_f \pm \text{SD}$ and justify any data you throw out with a 4D test. Show one sample calculation of initial concentrations of Fe³⁺ and SCN⁻ from dilution and equilibrium concentrations of FeSCN²⁺, using absorbance; then, show one ICE chart calculation for the equilibrium concentrations of Fe³⁺, and SCN⁻ and the related calculation of K_f .

This third section is where you not only present your data, but **use** the values you obtain as evidence in your reasoning. Statements like, "see data table for values" are not acceptable!

Remember: An argument is not just an answer to the question. It is a claim or conclusion supported by evidence with a rationale for why the evidence supports the claim or conclusion.

SAMPLE DATA TABLE

mL 0.00200 M Fe(NO ₃) ₃	mL 0.00200 <i>M</i> KSCN	mL H ₂ O	[Fe ³⁺] ₀	[SCN ⁻] ₀	abs	[FeSCN ²⁺] _{eq}	[Fe ³⁺] _{eq}	[SCN ⁻] _{eq}	K _f