Determining the Equilibrium Constant of a Chemical Reaction

Cautions

Potassium thiocyanate (KSCN) is hazardous.

Purpose

To determine the equilibrium constant, K_c, for the formation of a complex ion by measuring equilibrium concentrations of the reacting species involved.

Introduction

Many methods may be used to determine the equilibrium constant for a given system. A pH meter may be used to determine the acid dissociation constant, K_a, and it is also possible to determine the solubility product equilibrium constant, K_{sp}. However in this experiment the equilibrium constant, K_c, for the formation of a complex ion will be determined by measuring the concentrations of reactants in the reaction below. The equilibrium expression is also shown below.

$$\mathbf{Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons FeSCN^{2+}_{(aq)}} \qquad K_c = \frac{[FeSCN^{2+}]_E}{[Fe^{3+}]_E[SCN^-]_E}$$

The subscript "E" of the K_c expression indicates that each concentration is the equilibrium concentration

The $FeSCN^{2+}$ complex ion is a strongly colored species; therefore the reaction can be investigated using spectroscopy. In part A, a calibration curve, discussed below, will be constructed using $FeSCN^{2+}$ solutions of known concentration. Each standard solution contains an excess of Fe^{3+} to ensure all SCN^- in solution forms the $FeSCN^{2+}$ complex. Therefore, the concentration of $FeSCN^{2+}$ at equilibrium, $[FeSCN^{2+}]_E$, is equal to the initial concentration of SCN^-, $[SCN^-]_I$. The calibration curve will be used to determine the equilibrium concentration of $FeSCN^{2+}$, $[FeSCN^{2+}]_E$, of each sample (prepared in part B) containing similar concentrations of Fe^{3+} and SCN^- at equilibrium.

In part B, mixtures containing similar concentrations of Fe^{3+} and SCN^- as compared with part A will be prepared. Each solution will be allowed to reach equilibrium such that equations (1) and (2) are valid.

$$[Fe^{3+}]_I = [Fe^{3+}]_E + [FeSCN^{2+}]_E \qquad (1)$$

$$[SCN^-]_I = [SCN^-]_E + [FeSCN^{2+}]_E \qquad (2)$$

In equations (1) and (2), the subscript "I" indicates an initial concentration, and the subscript "E" indicates an equilibrium concentration.

Initial concentrations of iron ($[Fe^{3+}]_I$) and thiocyanate ($[SCN^-]_I$) ions can easily be determined based on the concentration of the stock solutions. The absorbance of the iron thiocyanate ion will be determined by spectroscopy and compared with the calibration curve prepared in part A to determine the equilibrium concentration of the ion ($[FeSCN^{2+}]_E$). The equilibrium concentrations of iron ($[Fe^{3+}]_E$) and thiocyanate ($[SCN^-]_E$) can be determined using equations (1) and (2).

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Short Review of Beer's Law & Spectroscopy

Beer's Law is defined below in equation (3).

$$\mathbf{A} = \boldsymbol{b}\ \mathbf{c}\ \boldsymbol{\varepsilon} \qquad (3)$$

In the equation, **A** is the measured absorbance of the sample, ***b*** is the path length of light through the sample, ***c*** is the concentration of the sample, and **ε** is a constant that depends on both wavelength and substance. A calibration curve, or Beer's Law plot, of absorbance (y-axis) versus concentration (x-axis) can be constructed from the absorbance and concentration data of standard solutions. A valid Beer's Law plot demonstrates a linear relationship between absorbance and concentration. A prepared calibration curve can be used to determine the concentration of an unknown solution from its measured absorbance.

Digital spectrophotometers in the laboratory measure the absorbance directly, but the analog spectrophotometers measure the percent transmittance. If an analog spectrophotometer is used, the absorbance (A) can be calculated from the recorded percent transmittance using equations (4) and (5). (T is the transmittance.)

$$\mathrm{T} = \frac{\textbf{percent transmittance}}{\mathbf{100}} \qquad (4)$$

$$\mathbf{A = -\log T} \qquad (5)$$

Procedure:

Initial Steps and Observations:

- Spectrophotometers should be turned on before lab and ready for use. Set the spectrophotometer wavelength to 460 nm.
- Record exact volumes (using correct number of significant figures) of the sample solutions in the data tables. Use a buret to deliver the Fe^{3+} and SCN^- solutions, and a graduated cylinder to measure HNO_3 and H_2O.
- Prepare all solutions in test tubes that are large enough to hold 20 mL.
- To thoroughly mix all solutions stopper and invert 5 times. Failure to adequately mix the solutions will result in a large error.
- Do **NOT** prepare solutions for part B until you have completed part A

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Part A: Construction of Beer's Law Plot

1. Prepare blank A and samples 1A – 4A using the **<u>0.10 M Fe^{3+} solution</u>** according to the volumes listed below. Since the measured volumes may vary slightly from the volumes in the table below, record the exact volume of each reagent used in Table 1 on page 5.

Sample	Volume (mL) of 0.004 M SCN^-	Volume (mL) of 0.10 M Fe^{3+}	Volume (mL) of 1.0 M HNO_3	Volume (mL) of Deionized H_2O
Blank A	0.00	10.00	5.0	5.0
1A	0.30	10.00	5.0	4.7
2A	0.60	10.00	5.0	4.4
3A	1.20	10.00	5.0	3.8
4A	2.00	10.00	5.0	3.0

2. Use the blank to set zero absorbance (digital spec 20s) or one hundred percent transmittance (analog spec 20s) at 460 nm on spectrophotometers.
3. Record the absorbance (on digital spec 20's) or percent transmittance (analog spec 20's) of each sample in Table 2 on page 5.
4. Calculate the $[FeSCN^{2+}]_E$ and place the value in Table 2 on page 5.
   - NOTE: $[FeSCN^{2+}]_E = [SCN^-]_I$ **only in part A**
   - Use a dilution calculation to calculate $[SCN^-]_I$. Dilution calculation: $M_1V_1 = M_2V_2$
5. Construct and attach to the data sheet a Beer's Law plot of absorbance versus $[FeSCN^{2+}]_E$.

Part B: Determination of the Equilibrium Constant

1. Prepare a blank sample B and samples 1B – 6B using the **<u>0.004 M Fe^{3+} solution</u>** according to the volumes listed below. Since the measured volumes may vary slightly from the volumes in the table below, record the exact volume of each reagent used in Table 3 on page 6.

Sample	Volume (mL) of 0.004 M SCN^-	Volume (mL) of 0.004 M Fe^{3+}	Volume (mL) of 1.0 M HNO_3	Volume (mL) of Deionized H_2O
Blank B	0.00	0.00	0.0	20.0
1B	2.00	8.00	5.0	5.0
2B	4.00	6.00	5.0	5.0
3B	5.00	5.00	5.0	5.0
4B	7.00	3.00	5.0	5.0
5B	2.00	3.00	5.0	10.0
6B	7.50	7.50	5.0	0.0

2. Use the blank to set zero absorbance (digital spec 20's) or one hundred percent transmittance (analog spec 20's) at 460 nm on spectrophotometers
3. Record the absorbance (on digital spec 20's) or percent transmittance (analog spec 20's) of each sample in Table 4 on page 6.
4. Calculate the respective concentrations and equilibrium constant (K_C) listed in Table 5 on page 7 for each sample.
5. Report an average equilibrium constant, K_c, on data sheet page 7.

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Data Sheet

Name: ___________________________________ **Lab Partner:** _______________________________

Actual concentration of $Fe(NO_3)_3$ stock solution used in **Part A** (approx. conc. = 0.10 M): _____________________

Actual concentration of $Fe(NO_3)_3$ stock solution used in **Part B** (approx. conc. = 0.004 M): ____________________

Actual concentration of KSCN stock solution used in **Part A & B** (approx. conc. = 0.004 M): ____________________

Part A: Construction of Beer's Law Plot

Table 1: Fill in the following table with the actual volumes used in Part A:

Sample	Volume (mL) of 0.004 M SCN^-	Volume (mL) of 0.10 M Fe^{3+}	Volume (mL) of 1.0 M HNO_3	Volume (mL) of Deionized H_2O	Total Volume of Solution (mL)
Blank A					
1A					
2A					
3A					
4A					

Table 2: Fill in the following table with the absorbance readings of each sample of Part A:

Sample	% Transmittance	Absorbance	$[FeSCN^{2+}]_E$ *
1A			
2A			
3A			
4A			

∗ **For Part A <u>only</u>:** $[FeSCN^{2+}]_E = [SCN^-]_I$

- Construct and attach a Beer's Law plot of absorbance versus $[FeSCN^{2+}]_E$. Give the best linear fit through the data.

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Part B: Determination of the Equilibrium Constant

Table 3: Fill in the following table with the actual volumes used in Part B:

Sample	Volume (mL) of 0.004 M SCN^-	Volume (mL) of 0.004 M Fe^{3+}	Volume (mL) of 1.0 M HNO_3	Volume (mL) of Deionized H_2O	Total Volume of Solution (mL)
Blank B					
1B					
2B					
3B					
4B					
5B					
6B					

Table 4: Fill in the following table with the absorbance readings of each sample of Part B:

Sample	% Transmittance	Absorbance	$[FeSCN^{2+}]_E$ *
1B			
2B			
3B			
4B			
5B			
6B			

∗ **For Part B:** $[FeSCN^{2+}]_E \neq [SCN^-]_I$. Use Beer's Law plot constructed from Part A and absorbance measured in Part B to determine $[FeSCN^{2+}]_E$ for Part B.

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Table 5: Fill in the following table with the calculated concentrations and equilibrium constant from Part B (Show sample calculations in the space provided below):

Sample	**$[SCN^{-}]_I$**	**$[FeSCN^{2+}]_E$**	**$[Fe^{3+}]_I$**	**$[Fe^{3+}]_E$**	**$[SCN^{-}]_E$**	**K_c**
1B						
2B						
3B						
4B						
5B						
6B						

Average K_C = ______________________

Calculations

- To calculate $[SCN^{-}]_I$ use a dilution calculation. ($M_1V_1 = M_2V_2$)
- For $[FeSCN^{2+}]_E$, recopy the values in the last column of Table 4.
- To calculate $[Fe^{3+}]_I$ use a dilution calculation. ($M_1V_1 = M_2V_2$)
- To calculate $[Fe^{3+}]_E$ use equation (1) on page 1.
- To calculate $[SCN^{-}]_E$ use equation (2) on page 1.
- To calculate K_c use expression on page 1.

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Post-Lab Assignment

Name: ____________________________________

1. On the Beer's Law plot, should the straight line pass through the origin ([$FeSCN^{2+}$] = 0; Absorbance = 0)? Explain your answer

2. Should the K_c values of the various trials be similar or vary considerably? Explain your answer.

3. Provide any sources of error that may have arisen from this experiment.

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Pre-Lab Assignment

Name: ____

A sample is prepared to use in today's experiment using the following volumes and concentrations of reagents:

2.00 mL 0.00400 M SCN^-	5.00 mL 1.00 M HNO_3
8.00 mL 0.00400 M Fe^{3+}	5.00 mL DI H_2O

It is determined that the equilibrium concentration of the iron thiocyanate ion ($[FeSCN^{2+}]_E$) is 1.75 X 10^{-4} M, use the introduction of this lab to calculate the concentration of the following species and the equilibrium constant.

$[Fe^{3+}]_I$ = ____________

$[SCN^-]_I$ = ____________

$[Fe^{3+}]_E$ = ____________

$[SCN^-]_E$ = ____________

K_c = ____________