Determining the Equilibrium Constant of a Chemical Reaction

Purpose

To determine the equilibrium constant, Kc (also called K_f) 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.

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

The $FeSCN^{2+}$ complex ion is a strongly colored species; therefore the reaction can be investigated using spectroscopy. In part A, a calibration curve will be constructed using $FeSCN^{2+}$ solutions of known concentration. Each standard solution contains a large excess of Fe^{3+} to ensure all SCN^- in solution forms the $FeSCN^{2+}$ complex. Therefore, the concentration of $FeSCN^{2+}$ at equilibrium is equal to the initial concentration of SCN^-. The calibration curve will be used to determine the equilibrium concentration of $FeSCN^{2+}$ 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^- will be prepared. Each solution will be allowed to reach equilibrium such that the following mass balance equations (1) and (2) are valid. With these equations and the initial concentration of the two ions the equilibrium concentrations can be determined.

$$[Fe^{3+}]_{initial} = [Fe^{3+}]_{eq} + [FeSCN^{2+}]_{eq} \qquad (1)$$

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

An alternate and probably more familiar way to determine equilibrium concentrations is the ICE box method. The ICE box method uses the same equations as above but arranges them in a chart like format.

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

Initial	I
Change	Δ
Equilibrium	Eq

The initial concentrations of iron Fe^{3+} and thiocyanate SCN^- ions can be easily determined from 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. The equilibrium concentrations can be found using the ICE box chart.

Short Review of Beer's Law & Spectroscopy

Beer's Law is defined below in equation: **A = a *b* c**

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 **a** is a constant that depends on both wavelength and substance. A linear 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 prepared calibration curve can be used to determine the concentration of an unknown solution from its measured absorbance.

Experimental Procedure:

General Instructions – *Read this BEFORE proceeding to Parts A and B.*

1. The SpectroVis Spectrometers and LabQuest units will be used for this experiment. The spectrometers need to be calibrated using the blank solutions for Part A and Part B respectively. See the procedure below for instructions on calibrating the spectrometer. The wavelength to be monitored for all samples is 460 nm.

2. There are four solutions used in this experiment. *Do not take more solution than you need and do not cross contaminate the solutions.*

   - Obtain two burets to deliver the 0.004 M Fe^{3+} and 0.004 M SCN^- solutions. *The burets must be clean prior to use. Be sure to rinse the buret with a few mL of the solution prior using.*
   - Use your 10.00 mL pipet for the 0.1 M Fe^{3+}.
   - Use a graduated cylinder for the 1.0 M HNO_3 and DI water. You can use a plastic pipet to accurately fill the cylinder.

   For each solution record the exact volumes you deliver in your data tables (and notebook) with the correct number of significant digits.

3. Prepare all solutions in test tubes large enough to hold 20 mL (provided).

4. Thoroughly mix all solutions by stoppering the tube and inverting at least five times. If the solutions are not properly mixed there will be significant error in your results.

5. DO NOT PREPARE solutions for part B until you have completed Part A.

Instrument Setup and Calibration

1. In the menu bar select **Sensors** then choose **Data Collection**. Select the dropdown arrow next to the Mode box and choose the **Time Based** option. Leave other settings as is. Tap OK.

2. In the menu bar select **Sensors**, then choose **Calibrate**, and select **USB:Spectrometer**. A calibration page should appear. Tap OK.

3. After the warm-up period obtain a cuvette filled with water to calibrate the spectrometer. Tap the **Finish Calibration** button. When the unit states calibration complete tap OK.

4. Back on the main screen, tap the panel labeled USB: Abs. Select **Change Wavelength** from the menu.

5. For the Selected Wavelength enter 460 nm. Tap **OK** when done.

Part A: Construction of Beer's Law Plot

1. Prepare blank A and samples 1A – 4A using the **0.10 M Fe^{3+} solution** 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 0.10 M Fe^{3+}	Volume (mL) of 0.004 M SCN^-	Volume (mL) of 1.0 M HNO_3	Volume (mL) of Deionized H_2O
Blank A	10.00	0.00	5.0	5.0
1A	10.00	0.30	5.0	4.7
2A	10.00	0.60	5.0	4.4
3A	10.00	1.20	5.0	3.8
4A	10.00	2.00	5.0	3.0

2. Calibrate the spectrometer with water. When calibrated obtain an absorbance reading for the Blank A solution. This will be used to correct for any background absorbance in the samples.

3. Record the absorbance of each sample in Table 2 (in your notebook).

4. Calculate the concentration of $[FeSCN^{2+}]_{eq}$ and place the value in Table 2 (in your notebook).

NOTE: a) $[FeSCN^{2+}]_{eq} = [SCN^-]_{initial.}$ ***This is true only for part A***
b) Use the dilution equation ($M_1V_1 = M_2V_2$) to calculate $[SCN^-]_{initial}$

5. Using Excel (or similar) generate a Beer's Law plot of absorbance versus $[FeSCN^{2+}]_{eq}$.

Part B: Determination of the Equilibrium Constant

1. Prepare a blank sample B and samples 1B – 6B using the **0.004 M Fe^{3+} solution** 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 (in your notebook).

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

2. Obtain an absorbance reading for the Blank B solution. This will be used to correct for any background absorbance in the samples.

3. Record the absorbance of each sample in Table 4 (in your notebook).

4. Calculate the concentration of $[Fe^{3+}]_{initial}$ and $[SCN^-]_{initial}$ and place the values in table 4 (in notebook).

Data Sheet

The following data and data tables should be entered neatly in a table in your notebook prior to lab:

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 0.10 M Fe^{3+}	Volume (mL) of 0.004 M SCN-	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					

Absorbance of Blank A ________________

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

Sample	Sample Absorbance (from Spectrometer)	Corrected Absorbance (Sample - blank)	*$[FeSCN^{2+}]_{eq}$ (from calculation)
1A			
2A			
3A			
4A			

* *Remember In part A only:* $[FeSCN^{2+}]_{eq} = [SCN^-]_{initial}$. *See Part A calculations*

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 Fe^{3+}**	**Volume (mL) of 0.004 M SCN-**	**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					

Absorbance of Blank B ________________

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

Sample	**$[Fe^{3+}]_{initial}$** (dilution calculation)	**$[SCN^-]_{initial}$** (dilution calculation)	**Sample Absorbance** (Spectrometer)	**Corrected Absorbance** (Sample - blank)	**$*[FeSCN^{2+}]_{eq}$** (from Beer's Law plot)
1B					
2B					
3B					
4B					
5B					
6B					

** Remember: In Part B: $[FeSCN2+]_{eq} \neq [SCN-]_{initial.}$ Use the Beer's Law plot from Part A and absorbance measured in Part B to determine $[FeSCN2+]_{eq}$ for Part B.*

Calculations

Part A

1. Calculate the concentration of the dilute thiocyanate solutions ($[SCN\text{-}]_{initial}$) using the concentration of the stock solution and the dilution equation ($M_1V_1 = M_2V_2$).

2. Make a graph of the corrected absorbance (y-axis) vs. *$[FeSCN^{2+}]_{eq}$ (x-axis). This is a Beer's law Plot. Add a linear best-fit trend line to the data. Include the equation for the best-fit line and the R^2 value.

** Remember In part A: $[FeSCN^{2+}]_{eq} = [SCN^-]_{initial}$*

Part B

3. Calculate the concentration of the dilute thiocyanate solutions ($[SCN\text{-}]_{initial}$) using the concentration of the stock solution and the dilution equation ($M_1V_1 = M_2V_2$).

4. Calculate the concentration of the dilute iron solutions ($[Fe^{3+}]_{initial}$) using the concentration of the stock solution and the dilution equation ($M_1V_1 = M_2V_2$).

(Remember in Part B $[Fe^{3+}]=0.004M$)

5. Using the corrected absorbance data for the six solutions in Part B and the equation for the linear fit to the Beer's Law plot in Part A, determine the concentration of iron thiocyanate complex at equilibrium. ($[FeSCN^{2+}]_{eq}$) for each solution.

Remember In Part B: $[FeSCN^{2+}]_{eq} \neq [SCN^-]_{initial.}$

5. Set up an ICE-box table similar to the one shown on the first page of this procedure. Using the initial concentrations of Fe^{3+} and SCN^- and the equilibrium value for the iron complex, determine equilibrium values for Fe^{3+} and SCN^-.

6. Calculate the value of Kc using the equilibrium values determined above. Repeat this for each of the six samples in part B.

7. Calculate an average value and the standard deviation for K_c.

8. Calculate the 95% confidence interval for K_c. Look up the true value in your textbook. *(These are referred to as K_f in your text, page A-12, Complex ion Formation constants in Water).* Does your calculated value agree with the true value at the 95% confidence interval?

Questions

1. In Part A the initial Fe^{3+} concentration was made to be very large compared to the initial thiocyanate concentration. Explain why?

2. In part A a blank solution was made containing Fe^{3+}, nitric acid and water but no thiocyanate.

   a) What is a blank solution? Why was it necessary to use a blank in this analysis?

   b) True or False - Once corrected with the blank solution the straight line on the Beer's law plot should pass through the origin. (In other words, zero concentration will give zero absorbance.) Explain your answer.

3. In part B the concentrations of Fe^{3+} and SCN^- for each of the six sample were all very different. As such should the calculated value of Kc be different as well or should it be the same (within error) for all samples. Explain.

4. The value of Kc from the data table in your textbook is 890. At the 95% confidence interval does your result agree or disagree with the published value. In other words does the accepted (true) value from your book fall in the range of your calculated value?

5. Your value is likely much lower. This has to something to do with the HNO_3 in solution. Use your knowledge of Le Chatlier's principle to explain why Kc is lower than the table value.