Using Spectrophotometric Methods to Determine an Equilibrium Constant

Prelab

1. What is the purpose of this experiment?

2. In step 11 of the procedure, it is stated that the absorbance of the solution increases as Fe³⁺ solution is added? Explain why using equation 3 and LeChatelier's Principle.

3. In steps 3, 5, 10 and 11, 10.00 mL of 2.00 x 10⁻³ M SCN⁻ is diluted to 100.0 mL and placed in a beaker. 0.100 M Fe³⁺ is added to this solution in 10 1.00 mL increments. Calculate [SCN⁻] and [Fe³⁺] in the 10 solutions. Do this in an attached spreadsheet (see page 5, you will use these values in Data Treatment and Discussion). You will only have data for columns A, C and D. You will measure the data for column B in the laboratory, so most of the columns will contain no data. Print the spreadsheet in landscape orientation. Adjust the column width to fit all the columns on one page. Include a calculation of the 5th solution in your notebook.
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Introduction

Chemical reactions do not typically go to completion. Reactions always reach equilibrium. When a system is at equilibrium, the rate at which products form from reactants is the same as the rate at which products are decomposing to produce reactants. For a general reaction,

\[
aA + bB \rightleftharpoons cC + dD
\]

the equilibrium expression is

\[
K = \frac{[C]^c[D]^d}{[A]^a[B]^b}
\]

where \( K \) is the equilibrium constant for the reaction at a given temperature. In this experiment, you will determine the equilibrium constant of the reaction

\[
\text{Fe}^{3+}(\text{aq}) + \text{SCN}^- (\text{aq}) \rightleftharpoons \text{FeSCN}^{2+}(\text{aq})
\]

Iron(III) ion reacts with thiocyanate ion (SCN\(^-\)) to produce the complex ion, thiocyanatoiron(III), which is **blood-red**. The equilibrium expression is

\[
K = \frac{[\text{FeSCN}^{2+}]_{eq}}{[\text{Fe}^{3+}]_{eq}[\text{SCN}^-]_{eq}}
\]

To determine the value of \( K \) for this reaction, the equilibrium concentrations of the three ions in solution must be determined. Beer’s Law will be used to measure the equilibrium concentration of thiocyanatoiron(III) ion, (from a known value of \( \varepsilon \) at 447 nm).

\[
[\text{FeSCN}^{2+}]_{eq} = \frac{A}{eb}
\]

To determine \([\text{Fe}^{3+}]_{eq}\) and \([\text{SCN}^-]_{eq}\), it can be assumed that the iron in the system must be present as either \(\text{Fe}^{3+}\) or \(\text{FeSCN}^{2+}\). Letting \([\text{Fe}^{3+}]_i\) represent the concentration of iron(III) **initially** (before reaction), then it can be written that

\[
[\text{Fe}^{3+}]_{eq} = [\text{Fe}^{3+}]_i - [\text{FeSCN}^{2+}]_{eq}
\]

Substituting the relationship from equation 5 for \([\text{FeSCN}^{2+}]_{eq}\), gives

\[
[\text{Fe}^{3+}]_{eq} = [\text{Fe}^{3+}]_i - \frac{A}{eb}
\]
Similar statements may be made about the thiocyanate ion. If \([\text{SCN}^-]_i\) represents the thiocyanate initially added to the system, then it can be concluded

\[
[\text{SCN}^-]_{eq} = [\text{SCN}^-]_i - \frac{A}{\varepsilon b}
\]  

(8)

Substituting equations 5, 7, and 8 into equation 4 gives

\[
K = \frac{A}{\varepsilon b}
\]

\[
\left[\text{Fe}^{3+}\right]_i - \frac{A}{\varepsilon b}
\]

\[
\left[\text{SCN}^-\right]_i - \frac{A}{\varepsilon b}
\]

(9)

In this experiment, \(b\) is 1.00 cm and \(\varepsilon\) of FeSCN\(^2+\) at 447 nm is \(5203 \text{ L/mole}\cdot\text{cm}\). By measuring the absorbance of mixtures of various \([\text{Fe}^{3+}]_i\) and \([\text{SCN}^-]_i\), \(K\) can be calculated.

NOTE:

Be very careful not to spill or discard any solution until the experiment is completely finished. All solution transfers must be done without losing any solution.

Part I  Measuring \(K\)

1. Start LoggerPro and make sure the netbook recognizes the interface.

2. Fill a cuvette at least \(\frac{1}{2}\) full with 0.5 M HNO\(_3\) to make a blank. Dry the cuvette with a Kimwipe. On the menu bar, select Experiment, Calibrate, Spectrometer:1. Wait for lamp to warm up. Place the blank in the SpectroVis. Line up the cuvette with the reference line. Click Finish Calibration. When it goes gray, click OK.

3. Pipet 10.00 mL of 2.00 \(\times 10^{-3}\) M KSCN solution (record the exact concentration) into a clean 250-mL beaker. Pipet 25.00 mL of 2.0 M HNO\(_3\) into the same beaker. Pipet 65.00 mL of distilled water into the beaker (2 x 20 mL + 25 mL).

4. Half-fill a clean, dry 50-mL beaker with 0.100 M Fe(NO\(_3\))\(_3\) (record the exact concentration).

5. Using a 1.00-mL pipet, add 1.00 mL of Fe(NO\(_3\))\(_3\) solution to the KSCN solution in the 250-mL beaker. Mix gently with a disposable pipet. Keep the pipet in the beaker for the remainder of the experiment.

6. Click to Configure Spectrometer. Under Collection Mode, select Absorbance vs Concentration. Check 447.0 nm as \(\lambda_{max}\). Click OK.
7. **Carefully** fill a clean, dry cuvette at least ½ full with the reddish solution using the disposable pipet. Keep the pipet in the beaker. Place the cuvette in the **SpectroVis**. Line up the cuvette with the reference line.

8. Click ![Collect](image) wait 10 seconds then click ![Keep](image). Enter 1 (the experiment #) in the dialog box asking you to enter the concentration, then click **OK**. Make a table in your notebook of **Experiment #** and **Absorbance**. Record the absorbance of experiment #1.

9. Without spilling, use the disposable dropper to return the contents of the cuvette **back into the beaker**. Do not rinse.

10. Repeat step 5. Draw solution into and out of the disposable pipet a few times after mixing the solution. Rinse the cuvette with some of the solution and return it to the beaker. **Do not discard or spill solution.** Mix, then fill the cuvette at least ½ full with the solution using the disposable dropper. Put the cuvette in the **SpectroVis**. Line up the cuvette with the reference line. Continue to steps 8 and 9. For concentration, enter 2 (as the experiment number). The absorbance should increase.

11. Repeat **step 10** eight more times (for a total of 10 data points). Enter 3, 4, 5, etc. as the concentration each time. The absorbance should increase each time, **but not linearly**. If it does not increase, notify the instructor. You will have 10 sets of data.

**Part II**

1. Test the effect of temperature on the **value** of the equilibrium constant by placing the cuvette containing solution 10 in a **50-mL beaker** of **hot** tapwater. Let it stand for 1 minute. Wipe off the cuvette and record the absorbance of the solution ( ![Keep](image) ).

**Part III**  **Determining Initial Conditions from Known K and Equilibrium Concentrations**

1. Pipet 10.00 mL of 2.00 x 10⁻³ M KSCN solution into a clean 250-mL beaker.

2. Pipet 25.00 mL of 2.0 M HNO₃ into this same beaker. Pipet 10.00 mL of the **unknown** Fe(NO₃)₃ solution. Pipet 55.00 mL of distilled water: 2 x 20 + 15.

3. Fill a clean, dry cuvette ½ full of the solution and record the absorbance ( ![Keep](image) ).

4. Click ![Stop](image) **Export** all the data to your flashdrive as a .csv file.
Data Treatment

Using Excel, set up 10 clearly labeled columns:

- **Column A**  Experiment # (1 through 10)
- **Column B**  Absorbance of Exp #
- **Column C**  \([\text{Fe}^{3+}]_i\) \((=A*0.100/(100+A))\)
- **Column D**  \([\text{SCN}^-]_i\) \((=0.0200/(100+A))\)
- **Column E**  \([\text{FeSCN}^{2+}]_{eq}\) \((=\text{A}/\epsilon \text{b} = \text{B}/5203)\)
- **Column F**  \([\text{Fe}^{3+}]_{eq}\) \((=\text{C}–\text{E})\)
- **Column G**  \([\text{SCN}^-]_{eq}\) \((=\text{D}–\text{E})\)
- **Column H**  
  \[K = \frac{[\text{FeSCN}^{2+}]_{eq}}{[\text{Fe}^{3+}]_{eq}[\text{SCN}^-]_{eq}}\] \((=\frac{\text{E}}{\text{F}\times\text{G}})\)
- **Column I**  
  \[x = \frac{\text{Absorbance}(\text{[Fe}^{3+}]_i + [\text{SCN}^-]_i)}{[\text{Fe}^{3+}]_i[\text{SCN}^-]_i} \] \((=\frac{\text{B}+\text{D}}{\text{C}\times\text{D}})\)
- **Column J**  
  \[y = \frac{\text{Absorbance}}{[\text{Fe}^{3+}]_i[\text{SCN}^-]_i} \] \((=\frac{\text{B}}{\text{C}\times\text{D}})\)

Give sample calculations of columns C-J (using the exact molarities of the iron(III) and SCN⁻ solutions).

Calculate the average of the 10 K values at the bottom of column H. For Part II, include the calculation of K for the hot solution (solution 11) on the spreadsheet below the average K.

Plot column J versus column I as an alternate way of determining K that does not rely on knowing the molar absorptivity. A linear trendline (not through 0,0) fit to the 10 data points has a slope of \(-\text{K}\). Compare this K to the average K (bottom of column H).

For Part III, use the average value of K (bottom of column H), the initial concentration of SCN⁻ in the 100-mL volumetric flask and the concentration of FeSCN^{2+} (from Beer’s law and the measured absorbance) to determine the original concentration of Fe^{3+} in the unknown solution.

Conclusion

Give the room temperature equilibrium constants (determined by the two methods), the higher temperature equilibrium constant and the concentration of the unknown Fe^{3+} solution. Also:

What does the magnitude of the average K (bottom of column H) suggest (in general terms) about the equilibrium position of the reaction (more toward reactants or toward products).

Using LeChatelier's Principle, the average K (bottom of column H), and the K of the warm solution, determine whether the reaction of Fe^{3+} with SCN⁻ to form FeSCN^{2+} is exothermic or endothermic. Explain.