Using Spectrophotometric Methods to Determine an Equilibrium Constant

Introduction

Not all chemical reactions go to completion. Usually chemical systems approach what is called 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,

\[ aA + bB \rightleftharpoons cC + dD \]  \hspace{1cm} (1)

the equilibrium expression is written as

\[ \frac{[C]^c [D]^d}{[A]^a [B]^b} = K \]  \hspace{1cm} (2)

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

\[ \text{Fe}^{3+}(\text{aq}) + \text{SCN}^-(\text{aq}) \rightleftharpoons \text{FeSCN}^{2+}(\text{aq}) \]  \hspace{1cm} (3)

The iron(III) ion reacts with the thiocyanate ion to produce the complex ion thiocyanatoiron(III) which is blood-red. Other complexes between iron(III) and the thiocyanate ion exist but the complex shown above will predominate since the iron(III) concentration will be high compared to the concentration of the thiocyanate ion. The equilibrium expression is

\[ K = \frac{[\text{FeSCN}^{2+}]_{\text{eq}}}{[\text{Fe}^{3+}]_{\text{eq}}[\text{SCN}^-]_{\text{eq}}} \]  \hspace{1cm} (4)

In order to determine the equilibrium constant 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) complex ion, where \( \varepsilon \) is known.

\[ [\text{FeSCN}^{2+}]_{\text{eq}} = \frac{A}{\varepsilon b} \]  \hspace{1cm} (5)

To determine \([\text{Fe}^{3+}]_{\text{eq}}\) and \([\text{SCN}^-]_{\text{eq}}\), 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 iron initially (before reaction), then it can be written that

\[ [\text{Fe}^{3+}]_{\text{eq}} = [\text{Fe}^{3+}]_i - [\text{FeSCN}^{2+}]_{\text{eq}} \]  \hspace{1cm} (6)

Substituting the relationship from equation 5 for \([\text{FeSCN}^{2+}]_{\text{eq}}\), gives
\[ [\text{Fe}^{3+}]_{eq} = [\text{Fe}^{3+}]_i - \frac{A}{\varepsilon b} \]  

(7)

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

\[
K = \frac{A}{\varepsilon b} \left( \frac{[\text{Fe}^{3+}]_i - \frac{A}{\varepsilon b}}{[\text{SCN}^-]_i - \frac{A}{\varepsilon b}} \right)
\]  

(9)

In this experiment, the pathlength of the cuvette is 1.00 cm and \(\varepsilon\) of FeSCN\(^{2+}\) at 447 nm is 5203 L/mole·cm. By measuring the absorbance of mixtures of various \([\text{Fe}^{3+}]_i\) and \([\text{SCN}^-]_i\), you will be able to calculate \(K\) for each experiment and an average \(K\).

NOTE:

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

Part I Measuring \(K\)

Procedure

1. Pipet 10.00 mL of 2.00 \(\times\) 10\(^{-3}\) M KSCN solution (record the exact concentration) into a clean 100.0 mL volumetric flask. Pipet 25.00 mL of 2.0 M HNO\(_3\) into the same volumetric flask. Add distilled water to the mark on the flask. Mix the contents thoroughly and transfer all of this solution to a clean, dry 250-mL beaker.

2. Obtain about 25 mL of 0.100 M Fe(NO\(_3\))\(_3\) in a clean, dry 50-mL beaker (record the exact concentration). Using a 1.00-mL pipet, add 1.00 mL of the Fe(NO\(_3\))\(_3\) solution to the 250-mL beaker containing the KSCN solution. Mix thoroughly by swirling the beaker. Carefully pour some of this solution into the 100-mL volumetric flask used in step 1, swirl, and carefully (without spilling) return the solution to the 250-mL beaker.

3. Set the Spectronic 20 to 447 nm. Set to 100% T (calibrate) with 0.5 M HNO\(_3\) solution as a blank. Using a disposable pipet, fill a cuvette with the solution from step 2 and measure the absorbance.
4. Without spilling, pour the contents of the cuvette back into the beaker. Use the same disposable pipet (above) to remove any drops of solution. Do not rinse.

5. Repeat steps 2 through 4 nine more times (for a total of 10 data points). Draw solution into and out of the disposable pipet a few times after swirling the beaker in step 2. Rinse the cuvette with some of the solution and return it to the beaker. **Do not discard.** Swirl again and continue to step 3. The absorbance should increase each time, **but not linearly.**

6. To test the effect of temperature on the **value** of the equilibrium constant, place the cuvette containing solution 10 in a 50-mL beaker of warm tapwater. Let it stand for 2 minutes and record the temperature. Wipe off the cuvette and record the absorbance of the solution.

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

**Procedure**

1. Pipet 10.00 mL of 2.00 x 10⁻³ M KSCN solution into a clean 100.0 mL volumetric flask.

2. Pipet 25.00 mL of 2.0 M HNO₃ into this same volumetric flask. Using a 10.00-mL pipet, add 10.00 mL of the unknown Fe(NO₃)₃ solution. Add distilled water to the mark on the flask.

3. Measure the absorbance at 447 nm after calibration.

**Questions**

1. Will the absorbance of the equilibrium mixture (at 447 nm) increase or decrease as Fe³⁺ solution is added? Explain using LeChatelier's principle on equation 3.

2. **In steps 1 and 2 of the procedure,** 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. Consider doing this in a spreadsheet (you will use these values in **Data Treatment and Discussion**), but include one sample calculation in the notebook.

**Data Treatment and Discussion**

Give a **sample** calculation of [Fe³⁺]ₐ (using the **exact** molarity of iron(III)) after addition to the SCN⁻ solution, [SCN⁻], (using the **exact** molarity of the SCN⁻) after the addition of the iron(III) solution, [FeSCN²⁺]ₐ from equation 5, where b = 1.00 cm and ε = 5203 L/mole·cm, [Fe³⁺]ₐ from equation 6, [SCN⁻]ₐ from equation 7 and K, from equation 8, of solution 1.

Using a spreadsheet, set up 7 **clearly labeled** columns with the following.
<table>
<thead>
<tr>
<th>Column 1</th>
<th>Absorbance, A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column 2</td>
<td>$[\text{Fe}^{3+}]_i$</td>
</tr>
<tr>
<td>Column 3</td>
<td>$[\text{SCN}^-]_i$</td>
</tr>
<tr>
<td>Column 4</td>
<td>$[\text{FeSCN}^{2+}]_{eq}$</td>
</tr>
<tr>
<td>Column 5</td>
<td>$[\text{Fe}^{3+}]_{eq}$</td>
</tr>
<tr>
<td>Column 6</td>
<td>$[\text{SCN}^-]_{eq}$</td>
</tr>
<tr>
<td>Column 7</td>
<td>$K = \frac{[\text{FeSCN}^{2+}]<em>{eq}}{[\text{Fe}^{3+}]</em>{eq}[\text{SCN}^-]_{eq}}$</td>
</tr>
</tbody>
</table>

Calculate, at the bottom of column 7, the average of the 10 K values. Include the calculation of K for the **warm** solution on the spreadsheet below the average K.

Using the average value of K, the initial concentration of SCN\(^-\) and the concentration of FeSCN\(^{2+}\) (from Beer’s law), determine the **original** concentration of Fe\(^{3+}\) in the unknown.

An alternate way of determining K that does not rely on knowing the molar absorptivity involves plotting

$$\frac{A}{[\text{Fe}^{3+}]_i[\text{SCN}^-]_i} \text{ (as } y \text{)} \text{ versus } \frac{A([\text{Fe}^{3+}]_i + [\text{SCN}^-]_i)}{[\text{Fe}^{3+}]_i[\text{SCN}^-]_i} \text{ (as } x \text{)}$$

A linear trendline (that does **not** go through 0,0) fit to the 10 data points has a slope of \( -K \). Compare this K to the average K of your previous calculations.

**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 address:

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

- **Using LeChatelier's Principle**, the average K, and the K of the warm solution, is the reaction of Fe\(^{3+}\) with SCN\(^-\) to form FeSCN\(^{2+}\) exothermic or endothermic. Explain.