Determination of an Equilibrium Constant

Purpose:
To determine the equilibrium constant, \( K_{eq} \), for the reaction shown below by spectroscopy.

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

Please Read:
The section in your lab manual titled "Volumetric Glassware". Pay particular attention to the section on measuring pipets.

Introduction to Chemical Equilibrium:
We are familiar with the typical chemical equation:

\[
a \ A + b \ B \longrightarrow c \ C + d \ D
\]  
(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 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:

\[
a \ A + b \ B \rightleftharpoons c \ C + d \ D
\]  
(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:

\[
K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}
\]  
(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.

An interesting point about equilibria: the same composition can be reached by mixing C and D or by mixing A and B. This is often a source of confusion. If the same composition can be reached from either side of the reaction equation, what then are the “reactants” and what are the “products”? For the purpose of writing equilibrium constants, reactants are those species on the left side (left of the equilibrium arrows) of the chemical equation as we have written it. Products are those species on the right side of the equation.

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 an acidic solution, these ions form a blood-red complex ion as shown in equation 4:
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\[
\text{Fe}^{3+}(aq) + \text{SCN}^- (aq) \rightleftharpoons \text{FeSCN}^{2+}(aq)
\]  \hspace{1cm} (4)

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

\[
K_{eq} = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]}
\]  \hspace{1cm} (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 FeSCN\textsuperscript{2+} at equilibrium by quantitatively measuring the red color of the FeSCN\textsuperscript{2+} ion. The techniques for measuring color is called spectroscopy, and will be discussed later in this document. For the following discussion, assume that the equilibrium concentration of FeSCN\textsuperscript{2+} can be measured.

If you know the initial (before equilibrium) concentrations of Fe\textsuperscript{3+} and SCN\textsuperscript{−}, 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 Fe\textsuperscript{3+} and 2.0 M SCN\textsuperscript{−}. 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 Fe\textsuperscript{3+} and 2.0 M SCN\textsuperscript{−} should have entries of 1.0 M under Fe\textsuperscript{3+} and SCN\textsuperscript{−} owing to dilution. The initial concentration of FeSCN\textsuperscript{2+} is 0. In our example, you might measure an equilibrium (final) concentration of 0.6 M FeSCN\textsuperscript{2+}. 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:

<table>
<thead>
<tr>
<th></th>
<th>Fe\textsuperscript{3+}</th>
<th>SCN\textsuperscript{−}</th>
<th>FeSCN\textsuperscript{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>1.0 M</td>
<td>1.0 M</td>
<td>0.0 M</td>
</tr>
<tr>
<td>Δ</td>
<td>−0.6 M</td>
<td>−0.6 M</td>
<td>+0.6 M</td>
</tr>
<tr>
<td>equilibrium (final)</td>
<td>0.4 M</td>
<td>0.4 M</td>
<td>0.6 M</td>
</tr>
</tbody>
</table>

In this experiment, 0.1 M HNO\textsubscript{3} serves as the solvent. The acid adds a large (compared to the reactants) amount of H\textsuperscript{+}. This prevents side reactions such as the formation of FeOH\textsuperscript{2+}, a brownish species that can affect the results. It also ensures that HSCN (from reaction of NaSCN and H\textsuperscript{+}) is essentially non-dissociated. The acid concentration is high enough that it is not affected by the reaction and remains constant at 0.1 M.
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Introduction to Spectroscopy:

Spectroscopy is the study of electromagnetic radiation. Visible light is one form of electromagnetic radiation. Spectroscopy can be used for determination of the concentrations of solutions.

If a solution is colored, the intensity of the color is proportional to the concentration of the colored solute. The relationship between color intensity and concentration is very important and was worked out, in various forms, by Pierre Bouguer (1729), Johann Lambert (1760), and August Beer (1852). In its modern form, it is most commonly called Beer's Law. Its mathematical form is shown below.

\[ A = \varepsilon l c \]  

where

- \( A \) = "absorbance", the amount of light absorbed by the sample.
- \( \varepsilon \) = “molar absorptivity” (a constant unique to that solute at that wavelength)
- \( l \) = path length, or distance the light travels through the solution
- \( c \) = concentration of solute

If the absorbances of solutions containing known concentrations of a colored solute are measured at a specified wavelength (essentially, color) of light, and the path length is kept constant, the relationship between concentration and absorbance is linear. A graph of this sort is called a calibration curve, and an example is shown below. The slope of the line, labeled "y" in the graph, is molar absorptivity. Absorbance is measured in absorbance units, abbreviated AU. Therefore, \( \varepsilon \) has units AU/M. Be careful with significant figures; \( \varepsilon \) must not have more digits than the terms used to determine it.

When \( \varepsilon \) is known, and absorbanced of solutions are measured, the Beer’s Law equation can be rearranged and solved for the concentrations of the solutions.

**FIGURE 1. Beer’s Law Plot for FeSCN\(^{2+}\)**

Absorbance of FeSCN\(^{2+}\) as a function of its concentration

\[ y = 3506.2x + 0.0421 \]

\[ R^2 = 0.9978 \]

Concentration of FeSCN\(^{2+}\) ion, mol/L
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It is important, when working with Beer’s Law plots, to specify the wavelength of light at which the measurements are made. In this experiment, you will work at 447 nm, red light at which the molar absorptivity of FeSCN$^{2+}$ is at its maximum.

In Part A of this experiment, you will prepare FeSCN$^{2+}$ solutions of known concentrations, measure their absorbances at 447 nm, and develop a calibration curve. A fair question is “How do I know the concentration of FeSCN$^{2+}$ in my standard solutions if it’s in equilibrium with Fe$^{3+}$ and SCN$^{1–}$?” In the standard solutions, the concentration of Fe$^{3+}$ is much higher than that of SCN$^{1–}$. 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$^{1–}$ used in preparing it. The absorbance measurement at 447 nm will correlate to the concentration of complex ion, and an accurate calibration curve (Beer’s Law plot) can be obtained.

In Part B, you will make equilibrium mixtures of Fe$^{3+}$, SCN$^{1–}$, and FeSCN$^{2+}$. You will determine the concentration of FeSCN$^{2+}$ by means of its absorbance at 447 nm. With this, you will be able to calculate the equilibrium concentrations of Fe$^{3+}$ and SCN$^{1–}$, and determine the equilibrium constant for the formation of FeSCN$^{2+}$.

Be careful, because the concentrations of the solutions used in Part A are different than those used in Part B. Your results will be very poor if you use the wrong solutions!

Safety and Waste Disposal:

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.

All of the solutions prepared in this experiment, as well as excess NaSCN solution, should be discarded in the waste container on the bench. You may wish to have a beaker in your work area to collect waste while you are doing the experiment. Make sure it is labeled.

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

1. Obtain 3 serological pipettes and a set of test tubes from the bench.
2. Set up a beaker for waste solution; make sure it is labeled.
3. Obtain about 10 mL of 0.100 M Fe(NO$_3$)$_3$ in 0.1 M HNO$_3$ in a clean, dry test tube. Obtain about 10 mL of 5.00 x $10^{-4}$ M NaSCN in 0.1 M HNO$_3$ in another test tube. Label the solutions.
4. Using pipettes, add the amounts of the Fe$^{3+}$ solution, SCN$^{1–}$ solution and water required for each run to test tubes. Refer to Table 1 on your data sheet for this. Use a stirring rod with a curved tip to mix the solution until the color is uniform.
5. Pour the first solution from the test tube into a cuvette (a special test tube used with the spectrometer). Measure and record the absorbance of the solution. When the measurement is complete, pour the solution from the cuvette back into the test tube. Measure the absorbances of all the solutions in turn.
6. Using a graphing calculator or the spreadsheet function in the computer, plot the absorbance of the FeSCN$^{2+}$ solutions as a function of their concentrations.
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7. If your plot is satisfactory (R^2 should be greater than 0.95) empty your cuvettes, rinse them, and dry them as thoroughly as you can. If you have a point or two that don't fit the line, make sure the color of the solution in question is reasonable. You may need to reread an absorbance or remake a standard to get a good calibration.

Part B: Preparation of the Equilibrium Mixtures and Absorbance Measurements

1. Obtain about 15 mL of 2.00 x 10^{-3} M Fe(NO_3)_3 in 0.1 M HNO_3 and 15 mL of 2.00 x 10^{-3} M NaSCN in 0.1 M HNO_3 in clean, dry graduated cylinders that have been labelled.

2. Condition your pipettes with the new solutions of Fe^{3+} and SCN^{1-}.

3. Using pipettes, add the amounts of the Fe^{3+} solution, SCN^{1-} solution and water required for each run to test tubes. Refer to Table 2 on your data sheet for this. Use a stirring rod with a curved tip to mix the solution until the color is uniform.

4. Measure and record the absorbance each solution as you did in Part A.

5. Use the absorbances for the solutions to determine the equilibrium concentration of FeSCN^{2+} for each run.

6. Fill in the reaction tables, and calculate K_{eq} for each run. Then determine the average K_{eq}, the range of values, and the range as a percent of the average.