Determination of the Equilibrium Constant for a Chemical Reaction

Background

When chemical substances react, the reaction typically does not go to completion. Rather, the system goes to some intermediate state in which both the reactants and products have concentrations that do not change with time. Such a system is said to be in chemical equilibrium. When in equilibrium at a particular temperature, a reaction mixture obeys the Law of Chemical Equilibrium, which imposes a condition on the concentrations of reactants and products. This condition is expressed in the equilibrium constant $K_c$ for the reaction.

In this experiment we will study the equilibrium properties of the reaction between iron (III) ion, $\text{Fe}^{3+}$, and thiocyanate ion, $\text{SCN}^-$:

$$\text{Fe}^{3+} (\text{aq}) + \text{SCN}^- (\text{aq}) \leftrightarrow \text{FeSCN}^{2+} (\text{aq})$$  \hspace{1cm} (1)

When solutions containing $\text{Fe}^{3+}$ ion and $\text{SCN}^-$ ion are mixed, Reaction 1 occurs to some extent, forming the iron (III) thiocyanate complex ion, $\text{FeSCN}^{2+}$, which has a deep red color. As a result of the reaction, the equilibrium amounts of $\text{Fe}^{3+}$ and $\text{SCN}^-$ will be less than they would have been if no reaction occurred; *for every mole of $\text{FeSCN}^{2+}$ that is formed, one mole of $\text{Fe}^{3+}$ and one mole of $\text{SCN}^-$ will react.* According to the Law of Chemical Equilibrium, the equilibrium constant expression $K_c$ for Reaction 1 is formulated as follows:

$$K_c = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]}$$  \hspace{1cm} (2)

The value of $K_c$ in Equation 2 is constant at a given temperature. This means that mixtures containing $\text{Fe}^{3+}$ and $\text{SCN}^-$ will react until Equation 2 is satisfied, so that the same value of the $K_c$ will be obtained no matter what initial amounts of $\text{Fe}^{3+}$ and $\text{SCN}^-$ were used.

The objectives of this experiment are: (1) to find $K_c$ for Reaction 2 for several mixtures of $\text{Fe}^{3+}$ and $\text{SCN}^-$ made up in varying proportions; and (2) to show that $K_c$ indeed has the same value in each of the mixtures. The reaction is a particularly good one to study because $K_c$ is of a convenient magnitude and the color of the $\text{FeSCN}^{2+}$ ion makes for an easy analysis of the equilibrium mixture.

The mixtures will be prepared by mixing solutions containing known concentrations of iron(III) nitrate, $\text{Fe(NO}_3)_3$, as a source of $\text{Fe}^{3+}$ ions and potassium thiocyanate, $\text{KSCN}$, as a source of $\text{SCN}^-$ ions. The color of the $\text{FeSCN}^{2+}$ ions formed will allow us to determine its equilibrium concentration using a spectrophotometer (discussed later). Knowing the initial concentrations of reactants in a mixture and the equilibrium concentration of $\text{FeSCN}^{2+}$, we can calculate the equilibrium concentrations of the rest of the pertinent species and then determine $K_c$.

Since the calculations required in this experiment may not be apparent, we will go through a step-by-step procedure by which they can be made. As a specific example, let us assume that we prepared a
mixture by mixing 10.0 mL of 2.00 x 10^{-3} M Fe(NO_3)_3 with 10.0 mL of 2.00 x 10^{-3} M KSCN. As a result of Reaction 1, some red FeSCN^{2+} ion is formed. By the method of analysis described later, its concentration at equilibrium is found to be 1.50 x 10^{-4} M. Our problem is to find $K_c$ for the reaction from this information. To do this we follow the five steps below:

1. Calculate the initial number of moles of each reactant in the mixture.
2. Determine the number of moles of product that were formed at equilibrium. Since the product was formed at the expense of reactants, we can calculate the amount of each reactant that was used up.
3. Calculate the number of moles of each reactant remaining in the equilibrium mixture.
4. Determine the concentration of each reactant.
5. Calculate $K_c$ for each reaction using Equation 2.

**Step 1: Finding the Initial Number of Moles of Each Reactant.** This requires relating the volumes and concentrations of the reagent solutions that were mixed to the numbers of moles of each reactant species in those solutions. By definition, the molarity of species $A$, $M_A$, is:

$$M_A = \frac{\text{Moles of } A}{\text{total volume of solution, } V_{\text{soln}} \text{ (in L)}}$$  

(3a)

Or

$$\text{Moles of } A = M_A \times V_{\text{soln}}$$  

(3b)

Using Equation 3b, it is easy to find the initial number of moles of Fe$^{3+}$ and SCN$^-$. For each solution the volume used was 10.0 mL, or 0.0100 L. The molarity of each of the solutions was 2.00 x 10^{-3} mol/L, so $M_{Fe^{3+}} = 2.00 \times 10^{-3} \text{ mol/L}$ and $M_{SCN^-} = 2.00 \times 10^{-3} \text{ mol/L}$. Therefore, in the reagent solutions, we find that

\[
\begin{align*}
\text{Initial moles Fe}^{3+} &= M_{Fe^{3+}} \times V_{Fe^{3+}} = 2.00 \times 10^{-3} \text{ mol/L} \times 0.0100 \text{ L} = 2.00 \times 10^{-5} \text{ mol} \\
\text{Initial moles SCN}^- &= M_{SCN^-} \times V_{SCN^-} = 2.00 \times 10^{-3} \text{ mol/L} \times 0.0100 \text{ L} = 2.00 \times 10^{-5} \text{ mol}
\end{align*}
\]

**Step 2: Finding the Number of Moles of Product Formed.** Here again we can use Equation 3b. Let’s say that the molarity of FeSCN$^{2+}$ was found to be 1.50 x 10^{-4} mol/L at equilibrium using the spectrophotometer (described later). The total volume of solution or the mixture at equilibrium is the sum of the two volumes that were mixed, and is 20.0 mL, or 0.0200 L. So,

$$\text{Moles FeSCN}^{2+} \text{ formed} = M_{FeSCN^{2+}} \times V_{\text{soln}} = 1.50 \times 10^{-4} \text{ mol/L} \times 0.0200 \text{ L} = 3.00 \times 10^{-6} \text{ mol}$$

The number of moles of Fe$^{3+}$ and SCN$^-$ that reacted, or were used up, in producing the FeSCN$^{2+}$ must also be both equal to 3.00 x 10^{-6} mol since, by Equation 1, it takes one mole Fe$^{3+}$ and one mole SCN$^-$ to make each mole of FeSCN$^{2+}$. Thus:

\[
\begin{align*}
\text{Number of moles Fe}^{3+} \text{ reacted} &= \text{Number of moles FeSCN}^{2+} \text{ formed} = 3.00 \times 10^{-6} \text{ mol} \\
\text{Number of moles SCN}^- \text{ reacted} &= \text{Number of moles FeSCN}^{2+} \text{ formed} = 3.00 \times 10^{-6} \text{ mol}
\end{align*}
\]

**Step 3: Finding the Number of Moles of Each Reactant Present at Equilibrium.** In Step 1 we determined that initially we had 2.00 x 10^{-5} moles Fe$^{3+}$ and 2.00 x 10^{-5} moles SCN$^-$ present. In Step
we found that in the reaction \(3.00 \times 10^{-6}\) moles \(\text{Fe}^{3+}\) and \(3.00 \times 10^{-6}\) moles \(\text{SCN}^-\) reacted. The number of moles present at equilibrium must equal the initial moles minus the number of moles that reacted. Therefore, at equilibrium,

\[
\text{Number of moles at equilibrium} = \text{initial no. moles} - \text{no. moles reacted}
\]

Equil. moles \(\text{Fe}^{3+}\) = \(2.00 \times 10^{-5} - 3.00 \times 10^{-6} = 1.70 \times 10^{-5}\) mol (4)

Equil. moles \(\text{SCN}^-\) = \(2.00 \times 10^{-5} - 3.00 \times 10^{-6} = 1.70 \times 10^{-5}\) mol

**Step 4 Finding the Concentrations of All Species at Equilibrium.** Experimentally, say we obtained the concentration of \(\text{FeSCN}^{2+}\) to be \(1.50 \times 10^{-4}\) M (as given in step 2). The number of moles of each of \(\text{Fe}^{3+}\) and \(\text{SCN}^-\) at equilibrium was obtained in Step 3. The volume of the mixture being studied was 20.0 mL, or 0.0200 L. So, at equilibrium, the concentrations of \(\text{Fe}^{3+}\) and \(\text{SCN}^-\) equal:

\[
[\text{Fe}^{3+}]_{eq} = M_{\text{Fe}^{3+}, eq} = \frac{\text{Equil. moles Fe}^{3+}/V_{\text{soln}}}{(1.70 \times 10^{-5}\text{ moles/0.0200L})} = 8.50 \times 10^{-4}\text{ mol/L}
\]

\[
[\text{SCN}^-]_{eq} = M_{\text{SCN}^-, eq} = \frac{\text{Equil. moles SCN}^-/V_{\text{soln}}}{(1.70 \times 10^{-5}\text{ moles/0.0200L})} = 8.50 \times 10^{-4}\text{ mol/L}
\]

**Step 5: Finding the Value of \(K_c\) for the Reaction.** Once the equilibrium concentrations of all the reactants and products are known, one needs merely to substitute into Equation 2 to determine \(K_c\):

\[
K_c = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} = \frac{1.50 \times 10^{-4}}{(8.50 \times 10^{-4})(8.50 \times 10^{-4})} = 204
\]

In this experiment you will obtain data similar to that shown in this example. The calculations involved in processing your data are completely analogous to those we have made. (However, your results will differ from the ones we obtained, since the data in our example were obtained at a different temperature and so relate to a different value of \(K_c\).)

In carrying out this analysis we made the assumption that the reaction which occurred was given by Equation 1. There is no inherent reason why the reaction might not have been:

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

Notice that in Reaction 5 2 moles of \(\text{SCN}^-\) reacted with one mole of \(\text{Fe}^{3+}\), so the reaction stoichiometry is 1:2. If you are interested in matters of this sort, you might ask how we know whether we are actually observing Reaction 1 or Reaction 5. The line of reasoning is the following. If Reaction 1 is occurring, \(K_c\) for that reaction as we calculate it should remain constant with different reagent mixtures. If, however, Reaction 5 is going on, \(K_c\) as calculated for that reaction should remain constant. In part B of the Data and Calculations section, we will assume that Reaction 5 occurs and make the analysis of \(K_c\)
on that basis. The results of the two sets of calculations should make it clear that Reaction 1 is the one that we are studying.

Two analytical methods can be used to determine $[\text{FeSCN}^{2+}]$ in the equilibrium mixtures. The more precise method uses a spectrophotometer, which measures the amount of light absorbed by the red complex at 447 nm, the wavelength at which the complex most strongly absorbs. The absorbance, $A$, of the complex is proportional to its concentration, $M$, and can be measured directly on the spectrophotometer:

$$ A = kM \quad (6) $$

Your instructor will show you how to operate the spectrophotometer, if available to your laboratory, and will provide you with a calibration curve or equation from which you can find $[\text{FeSCN}^{2+}]$ once you have determined the absorbance of your solutions.

In preparing the mixtures in this experiment we will maintain the concentration of $\text{H}^+$ ion at 0.5 M. The hydrogen ion does not participate directly in the reaction, but its presence is necessary to avoid the formation of brown-colored species such as $\text{FeOH}^{2+}$, which would interfere with the analysis of $[\text{FeSCN}^{2+}]$.

**Procedure**

In the hoods you’ll find the solutions of $2.00 \times 10^{-3}$ M KSCN and $2.00 \times 10^{-3}$ M Fe(NO$_3$)$_3$ in 1 M HNO$_3$. The volumes of reagents to be added to each test tube are summarized in Table 1. Note that the total volume in each test tube is 10.00 ml. Deliver the required amount of each chemical by means of a graduated or volumetric pipette, but do not mix the Fe$^+$ solution and SCN$^-$ solution until you are ready to use the spectrophotometer. Do one trial at a time.

The moment Fe(NO$_3$)$_3$ solution is in contact with KSCN solution the reaction starts.

<table>
<thead>
<tr>
<th>Table 1. Volumes of reagents needed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test Tube No.</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>-------------------------------------</td>
</tr>
<tr>
<td>Volume Fe(NO$_3$)$_3$ solution (mL)</td>
</tr>
<tr>
<td>Volume KSCN solution (mL)</td>
</tr>
<tr>
<td>Volume H$_2$O (mL)</td>
</tr>
</tbody>
</table>

Mix each solution thoroughly with the Vortexer or a glass stirring rod. Be sure to dry the stirring rod after mixing each solution.

**Determination of concentration of FeSCN$^{2+}$ by spectrophotometry**

Place a portion of the mixture from test tube 1 in a spectrophotometer cuvette, as demonstrated by your instructor, and measure the absorbance of the solution at 447 nm. Determine the concentration of FeSCN$^{2+}$ from the calibration curve provided for each instrument or from the equation furnished to
you. Record the value on the Data page. Repeat the measurement using the mixtures in each of the other 4 test tubes.

**DISPOSAL OF REACTION PRODUCTS**

In this experiment, reactant concentrations are very low. In most localities you can pour the contents of the test tubes down the sink when you have completed your measurements. However, consult your instructor for alternate disposal procedures.

**Processing the Data**

**Part A: Calculation of \( K_c \) assuming the reaction:** \( \text{Fe}^{3+}(aq) + \text{SCN}^-(aq) \leftrightarrow \text{FeSCN}^{2+}(aq) \)

This calculation is easily done by following Steps 1 through 5 in the procedure. Results are to be entered in the table either by hand or using Excel. If you are familiar with Excel, you may enter in the formulas directly and have the spreadsheet perform your calculations. Please keep all values to 3 significant figures.

**Step 1.** Find the initial number of moles of \( \text{Fe}^{3+} \) and \( \text{SCN}^- \) in the 5 mixtures. The initial number of moles is determined by the following: initial moles = \( M \times V \) (in L)

Enter these values into Columns 1 and 2 of the table.

**Step 2.** Determine the equilibrium concentration of \( \text{FeSCN}^{2+} \) from the measured absorbance and the calibration curve. Since the light absorbed is proportional to the concentration \( (A = k \times M) \):

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

where \( k \) is the slope of the line of the calibration curve. Enter this value into column 8 of the data table.

Next calculate the Equilibrium # of moles for \( \text{FeSCN}^{2+} \) in a similar fashion as Step 1:

\[
\text{Equil. moles FeSCN}^{2+} = [\text{FeSCN}^{2+}]_\text{eq} \times V_{\text{soln}} \text{ (in L)}
\]

Enter the value into column 5 of the data table. Please note that the equilibrium number of moles of \( \text{FeSCN}^{2+} \) equals the number of moles of \( \text{Fe}^{3+} \) and the number of moles \( \text{SCN}^- \) that reacted.

**Step 3.** Determine the equilibrium moles of \( \text{Fe}^{3+} \) and \( \text{SCN}^- \) by subtracting the moles that reacted for \( \text{Fe}^{3+} \) or \( \text{SCN}^- \) (from step 2) from the initial moles present: Equil. moles = Initial moles –Moles reacted. Enter these values into Columns 3 and 4 respectively.

**Step 4.** Determine the equilibrium concentrations of \( \text{Fe}^{3+} \) and \( \text{SCN}^- \), \( [\text{Fe}^{3+}]_\text{eq} \) and \( [\text{SCN}^-]_\text{eq} \), by dividing the equil. moles for each species by the total volume of the reaction mixture (total volume = 10.0 mL or 0.010 L): \( [\text{ ]}_\text{eq} = \text{equil. moles/V (in L)} \). Enter these values into Columns 6 and 7.

**Step 5** Calculate \( K_c \) for the reaction for each of the mixtures by substituting values for the equilibrium concentrations of \( \text{Fe}^{3+}, \text{SCN}^- \) and \( \text{FeSCN}^{2+} \) into the equilibrium expression for the reaction. Enter these values into the last column and find the average value of \( K_c \).
Part B: Calculations Assuming the formation of Fe(SCN)$_2^+$

In calculating $K_c$ in Part A, we assume, correctly, that the formula of the complex ion is Fe(SCN)$^{2+}$. It is by no means obvious that this is the case and one might have assumed that Fe(SCN)$^+$ was the species formed. The reaction would then be:

$$\text{Fe}^{3+} (aq) + 2\text{SCN}^- (aq) \leftrightarrow \text{Fe(SCN)}^+_2 (aq) \quad (5)$$

We can use the fact that the equilibrium constant must remain constant no matter what the initial concentrations of reactants or products are to help identify the correct equilibrium present. If we analyze the equilibrium system we have studied, assuming that 2 equivalents of SCN$^-$ bond to the Fe rather than 1 as suggested in equation (5) above, we should obtain non-constant values of $K_c$.

Using the same kind of procedure as in Part A, calculate $K_c$ for Mixtures 1, 3 and 5 on the basis that Fe(SCN)$^+_2$ is the formula of the complex ion formed by the reaction between Fe$^{3+}$ and SCN$^-$. The assumption of two SCN$^-$ reacting requires three changes in the calculation:

(i) Equilibrium $[\text{Fe(SCN)}^+_2]$ will equal one-half the $[\text{FeSCN}^{2+}]$ obtained for each solution in Part A.

(ii) The reaction requires that 2 moles of SCN$^-$ react. As a result, the change in # of moles will be $2 \times$ Eq. moles Fe(SCN)$^{2+}$. Therefore in calculating the equilibrium number of moles SCN$^-$ you will need to subtract (2*number of moles Fe(SCN)$^{2+}$) from the initial number of moles SCN$^-$. 

(iii) Since two moles of SCN$^-$ are required to react, this changes the equilibrium expression as well. The [SCN$^-]$ will need to be squared in the equilibrium expression.
Advance Study Assignment: Determination of the Equilibrium Constant for a Chemical Reaction

1. A student mixes 5.0 mL $2.00 \times 10^{-3}$ M Fe(NO$_3$)$_3$ with 5.0 mL $2.00 \times 10^{-3}$ M KSCN. She finds that in the equilibrium mixture the concentration of FeSCN$^{2+}$ is $1.2 \times 10^{-4}$ M. Find $K_c$ for the reaction

$$\text{Fe}^{3+} (aq) + \text{SCN}^- (aq) \leftrightarrow \text{FeSCN}^{2+} (aq)$$

**Step 1** Find the number of moles Fe$^{3+}$ and SCN$^-$ initially present. (Use Eq. 3.)

$\underline{\text{Sample calculation:}}$

$\underline{\text{Step 2}}$ How many moles of FeSCN$^{2+}$ are in the mixture at equilibrium? What is the volume of the equilibrium mixture? (Use Eq. 3.)

$\underline{\text{Sample calculation:}}$

How many moles of Fe$^{3+}$ and SCN$^-$ reacted to form FeSCN$^{2+}$?

$\underline{\text{Sample calculation:}}$

**Step 3** How many moles of Fe$^{3+}$ and SCN$^-$ remain in the solution at equilibrium? (Use Eq. 4 and the results of Steps 1 and 2.)

$\underline{\text{Sample calculation:}}$
Step 3 Sample calculation:

Step 4 What are the concentrations of Fe$^{3+}$, SCN$^-$, and FeSCN$^{2+}$ at equilibrium? What is the volume of the equilibrium mixture? (Use Eq. 3 and the results of Step 3.)

\[ [\text{Fe}^{3+}] = \underline{\text{__________}} \text{ M}; [\text{SCN}^-] = \underline{\text{__________}} \text{ M}; [\text{FeSCN}^{2+}] = \underline{\text{__________}} \text{ M} \]

Sample calculation:

\[ \underline{\text{____mL}} = \underline{\text{____ L}} \]

Step 5 What is the value of $K_c$ for the reaction? (Use Eq. 2 and the results of Step 4.)

$K_c = \underline{\text{______________}}$

Sample calculation:

2. Assume that the reaction studied in Problem 1 is Fe$^{3+}$(aq) + 2 SCN$^-$(aq) $\leftrightarrow$ Fe(SCN)$_2^+$ (aq). Find $K_c$ for this reaction, given the data in Problem 1, except that the equilibrium concentration of Fe(SCN)$_2^+$ is equal to $0.6 \times 10^{-4}$ M.

a. Formulate the expression for $K_c$ for the alternate reaction just cited.
b. Find $K_c$ as you did in Problem 1; take due account of the fact that two moles SCN$^-$ reacted per mole Fe(SCN)$^{2+}$ that formed.

**Step 1** Results are as in Problem 1.

**Step 2** How many moles of Fe(SCN)$_2^+$ are in the mixture at equilibrium (Use Eq. 3b)?

$\text{______________ moles Fe(SCN)$_2^+$}$

*Sample calculation:*

How many moles of Fe$^{3+}$ and SCN$^-$ reacted to form Fe(SCN)$_2^+$?

$\text{______________ moles Fe$^{3+}$ reacted ____________ moles SCN$^-$ reacted}$

*Sample calculation:*

**Step 3** How many moles of Fe$^{3+}$ and SCN$^-$ remain in solution at equilibrium? Use the results of Steps 1 and 2, noting that no. moles SCN$^-$ at equilibrium = original no. moles SCN$^-$ - (2 x no. moles Fe(SCN)$_2^+$).

$\text{______________ equil. moles Fe$^{3+}$ ____________equil. moles SCN$^-$}$

*Sample calculation:*

**Step 4** What are the concentrations of Fe$^{3+}$, SCN$^-$, and Fe(SCN)$_2^+$ at equilibrium? (Use Eq. 3 and the results of Step 3.)

$[\text{Fe}^{3+}] = \text{__________ M; [SCN}^-\text{]} = \text{__________ M; Fe(SCN)$_2^+$}] = \text{__________ M}$

*Sample calculation:*

**Step 5** Calculate $K_c$ on the basis that the alternate reaction occurs. (Use the answer to Part 2a.)

$K_c = \text{__________}$

*Sample calculation:*