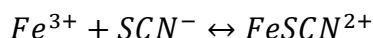# Experiment 7 – Determination of an Equilibrium Constant

Overview

In this experiment, we will examine a reaction that does not go to completion. Instead, it establishes an **equilibrium** which can be easily modeled. The reaction at which we will be looking is the aqueous reaction

$$Fe^{3+} + SCN^- \leftrightarrow FeSCN^{2+}$$

Chemical equilibrium is established when the rate at which the reaction progresses in the forward direction is equal to the rate at which the reverse reaction progresses. At this point, the concentrations of the reactants and products become constant, even though on a microscopy level, the forward and reverse reactions are still occurring. In this manner, chemical equilibrium is considered to be a **dynamic equilibrium**.

One the reaction has established equilibrium, the following relationship will hold, defined by the **equilibrium constant**, K.

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

In this experiment, we will establish the equilibrium in a reaction mixture, and measure the concentration of $[FeSCN^{2+}]_{eq}$ present. From this, the concentrations of $[Fe^{3+}]_{eq}$ and $[SCN^-]_{eq}$ can be calculated from their initial concentrations using the **mass-balance** expressions:

$$[Fe^{3+}]_{eq} = [Fe^{3+}]_0 - [FeSCN^{2+}]_{eq}$$
$$[SCN^-]_{eq} = [SCN^-]_0 - [FeSCN^{2+}]_{eq}$$

Finally, the value of the equilibrium constant can be determined.

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

Beer's Law

You might remember from *Experiment 2 – Light and Spectroscopy* that Beer's Law can be stated mathematically as

$$A = \varepsilon bc$$

where A is the absorbance, defined by

$$A = -\log\left(\frac{\%T}{100\%}\right)$$

with $\%T$ indicating the percentage of light that is transmitted through a sample. ε is the extinction coefficient (which depends on both the analyte and the wavelength of light), b is the absorbing path length, and c is the concentration of the absorbing species.

Example: Sally measures the absorbance of a sample in a 1 cm cuvette at 524 nm and finds it to be 0.462. What would the absorbance be if the concentration was doubled? What if the absorbing path length was increased to 2 cm?

Solution: Since

$$A = \varepsilon b c$$

Doubling the concentration (c) will double the absorbance. Hence, the new absorbance will be 0.924. Similarly, doubling the absorbing path length (b) will also double the absorbance. So the new absorbance would also be 0.924.

Experimental description

This experiment will be done in two parts. In the first part, you will determine the **extinction coefficient** to be used in Beer's Law to determine the concentration of [$FeSCN^{2+}$] in solution. Recall that Beer's Law is given by

$$A = \varepsilon b c$$

where A is the absorbance, ε is the extinction coefficient, b is the absorbing path length (the distance light travels through the sample), and c is the concentration of the sample. Measuring the absorbance of a sample of known concentration, and through a known path length, allows one to calculate the extinction coefficient.

Example: The absorbance of a sample with a known concentration of 1.00×10^{-3} M in a 1.00 cm cuvette is 0.395. Calculate the molar extinction coefficient for the sample at this wavelength.

Solution: We can use Beer's Law to solve the problem.

$$A = \varepsilon b c$$

$$0.395 = \varepsilon(1.00 \; cm)(1.00 \cdot 10^{-3} M)$$

$$\varepsilon = \frac{0.395}{(1.00 \ cm)(1.00 \cdot 10^{-3} M)} = 395 \ cm^{-1} M^{-1}$$

In the second part, you will measure the concentration $[FeSCN^{2+}]$ formed under several initial concentrations of $[Fe^{3+}]$ and $[SCN^-]$ in order to determine the equilibrium constant for the complexation reaction.

Example: A sample is found to have a molar extinction coefficient of 395 cm^{-1} M^{-1}. When measured in a 1.00 cm cuvette, the sample has an absorbance of 0.672. What is the concentration of the analyte in the sample?

Solution: Again, we use Beer's Law.

$$A = \varepsilon bc$$

$$0.672 = (394 \ cm^{-1} M^{-1})(1.0 \ cm)c$$

$$\frac{0.672}{(395 \ cm^{-1} M^{-1})(1.00 \ cm)} = c = 1.7\underline{0}13 \cdot 10^{-3} M$$

Part I – Determination of ε

Into a large test tube, pipet 10.00 mL of 0.200 M $Fe(NO_3)_3$ in 1 M HNO_3. To this add 2.00 mL of 0.00200 M KSCN, and 8.00 mL of water. Mix and allow the system to come to equilibrium. In this case, the initial concentration of $[Fe^{3+}]_0$ greatly exceeds that of $[SCN^-]_0$, so that at equilibrium, the concentration of $[SCN^-]_{eq}$ is negligibly small, and the equilibrium concentration of $[FeSCN^{2+}]_{eq}$ is equal to $[SCN^-]_0$.

Pour a small amount of your equilibrium mixture into a cuvette and measure the absorbance at 447 nm. (You may wish to look at the total absorption spectrum of the sample to confirm that 447 nm is an appropriate wavelength at which to perform measurements.)

Keeping in mind that the total volume of your equilibrium sample is 20.00 mL, calculate the concentration of thiocyanate $[SCN^-]_0$, which is equal to the concentration of the complex $[FeSCN^{2+}]_{eq}$ at equilibrium. Use your measured absorbance to determine the value of the extinction coefficient for the complex.

Part II – Equilibrium Measurements

Label five medium sized test tubes 1-5. In each, you will create an equilibrium mixture and measure the equilibrium concentration of the complex $[FeSCN^{2+}]_{eq}$ formed in each mixture. You can use the following set of recipes.

Sample	0.00200 M Fe(NO$_3$)$_3$	0.00200 M KSCN	mL H$_2$O
1	5.00 mL	1.00 mL	4.00 mL
2	5.00 mL	2.00 mL	3.00 mL
3	5.00 mL	3.00 mL	2.00 mL
4	5.00 mL	4.00 mL	1.00 mL
5	5.00 mL	5.00 mL	0

Mix the solutions in a 10.00 mL volumetric flask, by first adding the Fe(NO$_3$)$_3$ solution, then the KSCN solution, then bringing the mixture to volume with deionized H$_2$O. Transfer the resulting mixture to a test tube to store until measuring. After mixing all of the equilibrium mixtures (and allowing them to come to equilibrium), measure the absorbance of each sample at 447 nm.

Vocabulary and Concepts

Beer's Law 2
chemical equilibrium 1
dynamic equilibrium 1
equilibrium 1
equilibrium constant.................................... 1
extinction coefficient 2
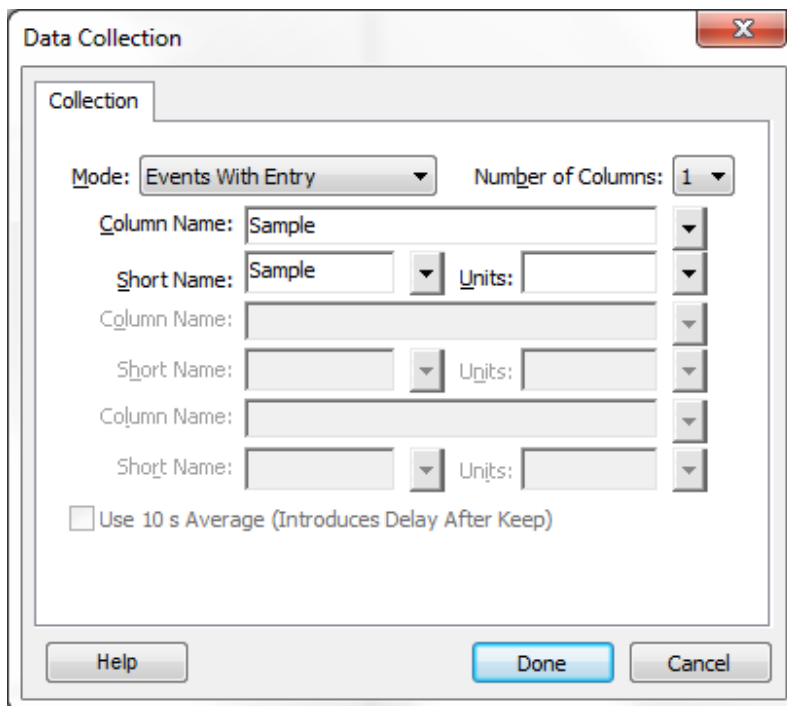mass-balance 1

References

[1] J. Randall, Advanced Chemistry with Vernier, 3rd ed., Beaverton, OR: Vernier Software and Technology, 2013.

Instructions for the Vernier SpectraVis+

1. Use a USB cable to connect the Spectrometer to the computer. Choose New from the File menu.
2. To calibrate the Spectrometer, place the blank cuvette into the cuvette slot of the Spectrometer, choose "Calibrate Spectrometer" from the Experiment menu. Wait for the Spectrometer to warm up, then click "OK". Follow the instructions.
3. Determine the optimum wavelength for the equilibrium mixture and set up the mode of data collection.

a. Empty the water from the blank cuvette. Using the solution in Sample 1, rinse the cuvette twice with ~1 mL amounts and then fill it 3/4 full. Wipe the outside with a tissue and place the cuvette in the Spectrometer.

b. Click "Collect". The absorbance *vs.* wavelength spectrum will be displayed. Note that one area of the graph contains a peak absorbance. Click "Stop".

c. To save your graph of absorbance *vs.* wavelength, select Store Latest Run from the Experiment menu.

d. Click the Configure Spectrometer Data Collection icon, , on the toolbar. A dialog box will appear.

e. Select "Absorbance" under Set Collection Mode. The wavelength of maximum absorbance (λ_{max}) is automatically identified. The λ_{max} should be 400- 480 nm for $FeSCN^{2+}$. Click "OK".

4. Collect Absorbance data for each of the samples you have prepared.

a. Under the "Experiment" menu, click on "Data Collection". Edit the column name, short name, and units as shown.

b. Click "Collect" to begin collecting data.

c. The first sample should still be in the spectrometer.

d. Place each sample in the rinsed cuvette (as you did for the first sample in step 3a) and wait for the absorbance to stabilize. When it does, click the "Keep" icon to record that point. You will be asked for the sample number. Record the absorbance you measure.

5. When all of the data points have been recorded, Click "Stop" to stop the spectrometer.

Pre-Laboratory Assignment – Equilibrium Constant

Name _____   Section _____

For the prelaboratory assignment, you will need to calculate the initial concentrations of $[Fe^{3+}]_0$ and $[SCN^-]_0$ for samples 1-5 that you will use in Part II of the experiment. The recipes for these samples are

Sample	0.00200 M Fe(NO₃)₃	0.00200 M KSCN	mL H₂O
1	5.00 mL	1.00 mL	4.00 mL
2	5.00 mL	2.00 mL	3.00 mL
3	5.00 mL	3.00 mL	2.00 mL
4	5.00 mL	4.00 mL	1.00 mL
5	5.00 mL	5.00 mL	0

So, for example, the concentration of $[SCN^-]_0$ in sample 1 is given by
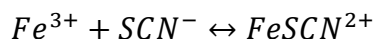
$$\frac{(1.00\ mL)(0.00200\ M)}{10.00\ mL} = 0.000200\ M$$

And for $[Fe^{3+}]_0$, the concentration is given by:

$$\frac{(5.00\ mL)(0.00200\ M)}{10.00\ mL} = 0.00100\ M$$

Sample	$[Fe^{3+}]_0$ (M)	$[SCN^-]_0$ (M)
1		
2		
3		
4		
5		

If the reaction mixture for

$$Fe^{3+} + SCN^- \leftrightarrow FeSCN^{2+}$$

Is prepared to have a large excess of Fe^{3+}, how do we know that $[FeSCN^{2+}]_{eq} = [SCN^-]_0$?

Prelaboratory assignment (continued)

Eshaq measures the absorbance at 447 nm of a sample prepared by mixing 10.00 mL of 0.200 M $Fe(NO_3)_3$ in 1 M HNO_3 with 2.00 mL of 0.00200 M KSCN, and 8.00 mL of water. He prepares the sample in a test tube, and then transfers some of the solution to a 1.00 cm cuvette. The absorbance at 447 nm is 0.702.

Assuming that the reaction goes to completion (due to the large difference in concentration of Fe^{3+} and SCN^-, what is the concentration of $[FeSCN^{2+}]$ in the test solution?

$$[FeSCN^{2+}] = \text{_____} \text{ M}$$

What is the value of the molar extinction coefficient for $[FeSCN^{2+}]$ at 447 nm?

$$\varepsilon = \text{_____} \text{ cm}^{-1} \text{ M}^{-1}$$

After determining the extinction coefficient, Eshaq measures the absorbance of a solution prepared by mixing 5.00 mL of 0.00200 M Fe^{3+}, 1.00 mL of 0.00200 M SCN^-, and 4.00 mL of water. He measures the absorbance to be 0.152. Based on this data

$$[FeSCN^{2+}]_{eq} = \text{_____} \text{ M}$$

$$[Fe^{3+}]_{eq} = \text{_____} \text{ M}$$

$$[SCN^-]_{eq} = \text{_____} \text{ M}$$

K_{eq} is given by

$$K_{eq} = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$$

$$K_{eq} = \text{_____} \text{ M}^{-1}$$

Report Sheet – Determination of an Equilibrium Constant

Name _____   Date _____

Lab Partner(s) _____

Part I – Determining the Extinction Coefficient

$[SCN^-]_0$ (diluted thiocyanate concentration)   _____

$[FeSCN^{2+}]_{eq}$ _____

Absorbance at 447 nm   _____

Extinction coefficient (ε)   _____

Part II – Equilibrium Mixtures

Based on your data, complete the following tables:

Sample	$[Fe^{3+}]_0$ (M)	$[SCN^-]_0$ (M)
1		
2		
3		
4		
5		

Sample	Abs	$[FeSCN^{2+}]_{eq}$ (M)	$[Fe^{3+}]_{eq}$ (M)	$[SCN^-]_{eq}$ (M)	$K = \dfrac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$
1					
2					
3					
4					
5					

Average value for K: