Purpose

To use spectrophotometry to determine the equilibrium constant of a reaction.

Learning Objectives

Use absorbance values of standard solutions to set up a calibration curve.

Determine equilibrium concentrations by comparison to the standard curve.

Apply the information from a balanced chemical equation and data obtained in the laboratory to determine the concentrations of reactants and products at equilibrium.

Calculate the value of the equilibrium constant using data obtained in the laboratory.

Laboratory Skills

Prepare solutions of appropriate concentrations for a calibration curve.

Equipment

- 25 mL volumetric flask
- Six 50 mL Erlenmeyer flasks or beakers
- 10 mL volumetric flasks
- Five 150 mm test tubes
- 10 mL pipet
- Two 5 mL pipets
- Spectrophotometer or colorimeter
- Cuvettes
- Kimwipes

Chemicals

- 0.200 M $Fe(NO_3)_3$ in 0.1 M HNO_3
- 2.00×10^{-3} M $Fe(NO_3)_3$ in 0.1 M HNO_3
- 1.00×10^{-3} M NaSCN in 0.1 M HNO_3
- 2.00×10^{-3} M NaSCN in 0.1 M HNO_3
- 0.1 M HNO_3

Introduction

Reversible Reactions and Equilibrium

Most reactions do not go completely to products. Instead, they reach a state where the rate of the forward reaction equals the rate of the reverse reaction called the **equilibrium state**. Since the rates of the forward reaction and reverse reaction are equal, the net change in reactant and product concentrations over time is equal to zero. To an observer, it would look like the reaction has stopped. However, this is not the case. The reaction is still proceeding, just the rates of forward and reverse reactions exactly cancel.

Reversible reactions are indicated using two arrows facing in opposite directions, as shown in a generic chemical reaction shown in Reaction KEQ.1:

$$\mathrm{aA} + \mathrm{bB} \rightleftharpoons \mathrm{cC} + \mathrm{dD} \qquad \text{(Reaction KEQ.1)}$$

In Reaction KEQ.1, the lowercase letters represent coefficients and the uppercase letters represent chemical formulas. A reaction at equilibrium follows the **law of mass action**, which gives the relationship between concentrations of the reactants and products at equilibrium. According to the law of mass action, the relationship between concentrations of reactants and products *at equilibrium* for the above reaction is given in Equation KEQ.1:

$$K_{\mathrm{eq}} = \frac{[\mathrm{C}]_{\mathrm{eq}}^{c}\,[\mathrm{D}]_{\mathrm{eq}}^{d}}{[\mathrm{A}]_{\mathrm{eq}}^{a}\,[\mathrm{B}]_{\mathrm{eq}}^{b}} \qquad \text{(Equation KEQ.1)}$$

The subscript “eq” in the equation refers to concentrations of reactants and products at equilibrium. Once a reaction has reached equilibrium, the concentrations of reactants and products do not change. The value of the equilibrium constant changes only with temperature. As long as the temperature remains constant, the value of the equilibrium constant does not change.

Beer's Law and Spectrophotometry

Chromophores (colorful substances) absorb certain wavelengths of light. A common laboratory instrument called a spectrophotometer is used to measure the concentration of light-absorbing chemicals in solution. Spectrophotometers contain a light source, a monochromator to direct the wavelength of interest through the sample, a sample compartment, and a detector (Figure KEQ.1). The detector measures the amount of light coming through a sample from the light source.

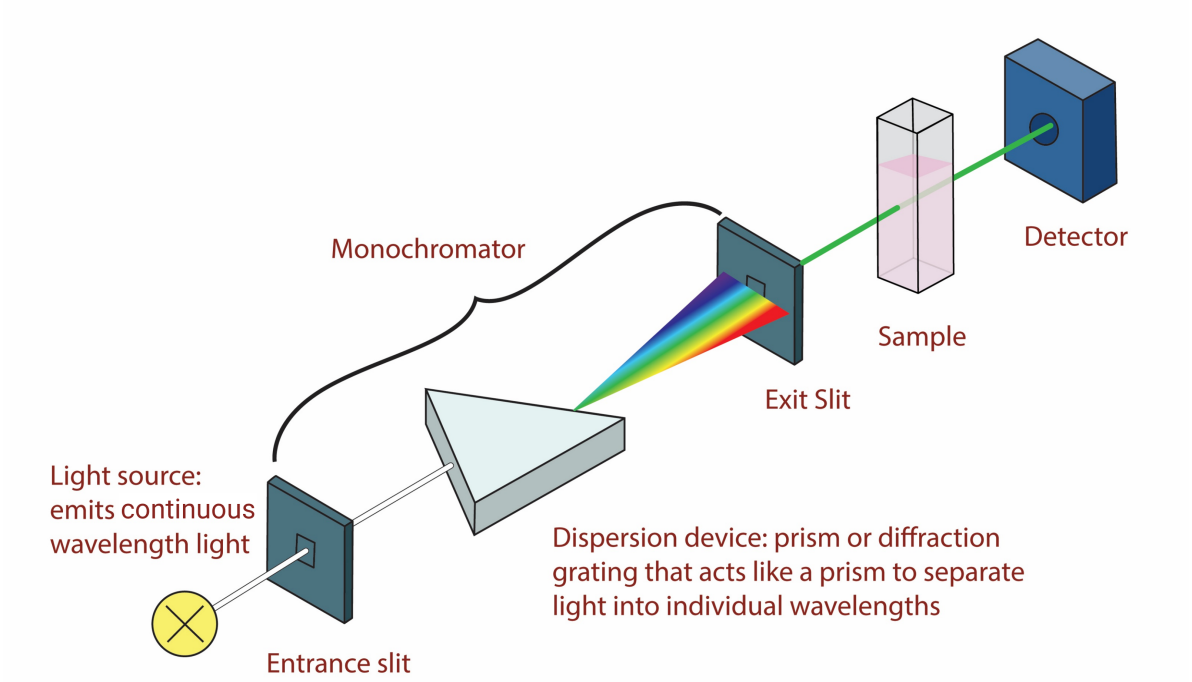

Figure KEQ.1: Schematic of a spectrophotometer showing the light path from the source to the detector.

The light source emits a certain amount of light energy, referred to as irradiance, ***I***. The light that passes through the sample is the transmittance, which is defined in Equation KEQ.2 as the fraction of the irradiance that passes through the sample. I_0 is the amount of light that is detected when there is no sample to absorb it and $I - t$ is the light that passes through the sample.

$$T = \frac{I_t}{I_0} \qquad \text{(Equation KEQ.2)}$$

Solutions are transferred into a container called a cuvette, which is then placed in the sample chamber of the spectrophotometer. A light source shines light of a specific wavelength through the sample to a light detector. The detector measures transmittance and converts that to absorbance using Equation KEQ.3.

$$A = -\log\left(\frac{1}{T}\right) \qquad \text{(Equation KEQ.3)}$$

The resulting absorbance value is related to the concentration of the light-absorbing species or chromophore in the sample solution. For any particular light-absorbing substance, absorbance is measured over a range of wavelengths to determine the wavelength absorbed most strongly, known as λ_{max}. Absorbance at this wavelength can then be used to quantify the amount of that chromophore present in a solution.

Beer's Law equates the amount of light absorbed by a sample, A, to the product of three terms, one of which is the concentration, c, of the light absorbing substance. Equation KEQ.4 indicates a direct relationship between the absorbance of light and the concentration of the chromophore. That is, the absorbance of light increases as the concentration increases. Visually, this means that a solution appears darker if there is more of a colored chemical present. The other factors in Equation KEQ.4 are the molar absorptivity (ϵ), which is unique for each chromophore and b, the path length of the light through the sample, typically one centimeter.

$$A = \epsilon bc \qquad \text{(Equation KEQ.4)}$$

Beer's Law is a useful relationship to determine the concentration of a chemical in solution using a spectrophotometer to measure the absorbance. To be able to measure a concentration in an unknown solution, you must first measure the absorbance values of several solutions of known concentration and create a standard curve. The slope of the standard curve provides is the molar absorptivity value (ϵ), which can be used to calculate the concentration of a solution of unknown concentration from its absorbance.

Example KEQ.1

Students measured the absorbance of standard solutions of a chromophore, graphed the data and determined that the their standard curve is $y = 3.6 \times 10^5\ \mathrm{M^{-1}cm^{-1}}x + 0$, where y is absorbance and x is molar concentration. They then measured the absorbance of a solution of unknown concentration of that chromophore at 422 nm and found it to be 0.402. Use their data to determine the molar concentration of the solution.

Start by rearranging the equation for the standard curve for x, concentration.

$$\text{molar concentration} = \frac{\text{absorbance}}{3.6 \times 10^5\ \mathrm{M^{-1}cm^{-1}}}$$

Replace the variables with values given in the problem:

$$\text{molar concentration} = \frac{0.402}{3.6 \times 10^5\ \mathrm{M^{-1}cm^{-1}}\ (1\ \mathrm{cm})} = 1.12 \times 10^{-6}\ \mathrm{M}$$

The concentration of the unknown chromophore solution is 1.12×10^{-6} M or 1.12 μM.

The Experiment

In this activity, you will determine the equilibrium constant for the formation of a colorful complex ion, the thiocyanatoiron(III) complex ion, $FeNCS^{2+}$ (Reaction KEQ.2) from aqueous solutions of Fe^{3+} and SCN^-, both of which are colorless.

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeNCS^{2+}(aq) \qquad \text{(Reaction KEQ.2)}$$

The formula for the thiocyanate ion is typically given as SCN^-, however, because thiocyanate is bonded to the iron ion through the nitrogen atom, the formula for the complex is correctly written $FeNCS^{2+}$. While the reactants are colorless solutions, the product complex is a deep red color with a $\lambda_{max} = 447$ nm. The equilibrium constant for this system is given in Equation KEQ.5:

$$K_{eq} = \frac{[FeNCS^{2+}]}{[Fe^{3+}][SCN^-]} \qquad \text{(Equation KEQ.5)}$$

In part A you will prepare a set of standard solutions of the $FeNCS^{2+}$ ion by combining a specific volume of 0.2 M Fe^{3+} and various volumes of 0.001 M SCN^-. Each solution contains a large excess of Fe^{3+}, which shifts the equilibrium far to the right, causing nearly all of the SCN^- to react to form the $FeNCS^{2+}$ ion. Thus, the concentration of $FeNCS^{2+}$ ion in the standard solutions is equal to the concentration of SCN^- in each solution (Figure KEQ.2).

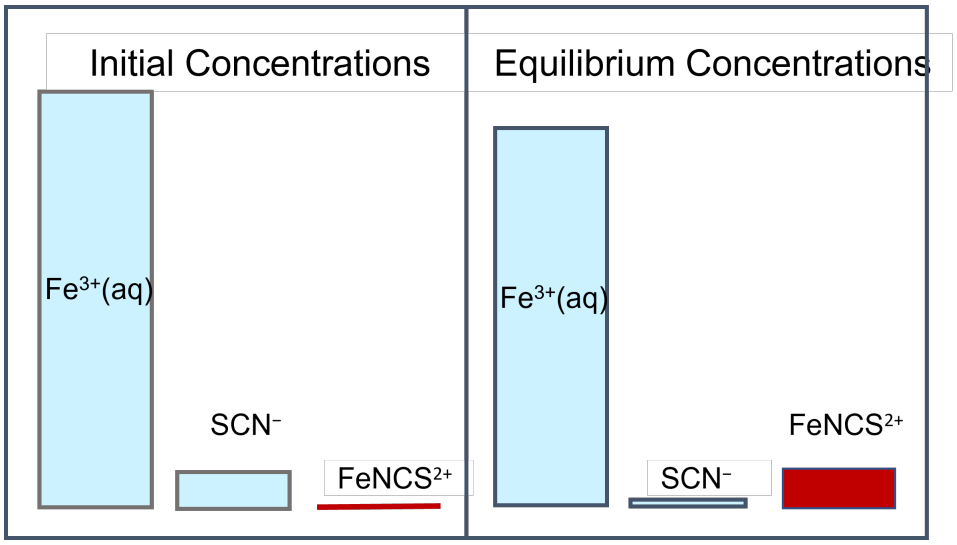

Figure KEQ.2: A large excess of one reactant shifts the equilibrium toward the product, making the product concentration equal to the concentration of the reactant NOT present in excess.

You will determine the absorbance of each solution and use the data and Excel (or other spreadsheet software) to make a calibration curve.

In part B, you will make a series of solutions using a specific volume of 0.002 M M Fe^{3+} and various volumes of 0.002 M SCN^-. Because these solutions contain similar initial concentrations of both reactants, the concentration of the complex ion product is determined by the equilibrium. (Figure KEQ.3).

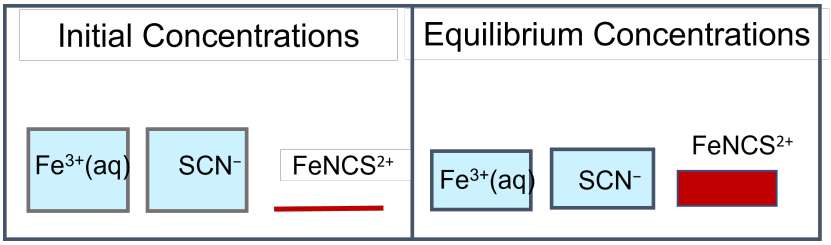

Figure KEQ.3: When similar amounts of the reactants are combined, the concentration of product is determined by the equilibrium.

You will determine the absorbance of each solution and use the calibration curve from Part A to determine the concentration of $FeNCS^{2+}$ ion in each solution. You will then use ICE analyses to determine the equilibrium concentrations of each solution and the equilibrium concentrations to determine the value of the equilibrium constant.

Data Analysis

A. Making the Calibration Curve

Once you have the absorbance values for the five standard solutions, you will create an Excel file and analyze your data for a linear trend of absorbance vs. concentration. Recall that Beer's law is $A = \epsilon bc$, where ϵ is the molar absorptivity of the chromophore. The slope of the calibration curve is the molar absorptivity coefficient for the $FeNCS^{2+}$ ion. Rearrange the equation to solve for $[FeNCS^{2+}]$ and determine the concentration for each solution in part B.

B. Determining the Equilibrium Constant

For each solution in part B, you will make an ICE table (See Labflow video "Equilibrium Constants And Calculations") to determine the concentrations of all species at equilibrium, following Example KEQ.2:

Example KEQ.2

Using her calibration curve, a student determined that the test solution made by mixing equal volumes of 2.00×10^{-3} M Fe^{3+} and 2.00×10^{-3} M SCN^- resulted in $[FeNCS^{2+}] = 1.70 \times 10^{-4}$ M. She correctly noted that mixing equal volumes reduces the concentration of each solute to 1/2 the original concentration. Then, she set up an ICE table to calculate the equilibrium concentrations of both reactants:

	$[Fe^{3+}]$	$[SCN^-]$	$\rightleftharpoons$	$[FeNCS^{2+}]$
Initial	1.00×10^{-3} M	1.00×10^{-3} M		0 M
Change	$-x$	$-x$		$+x$
Equilibrium	$0.001\text{M} - 1.7 \times 10^{-4}$	$0.001\text{M} - 1.7 \times 10^{-4}$		1.7×10^{-4} M

Next, she used the equilibrium concentrations from her ICE table to calculate the value of the equilibrium constant using Equation KEQ.5:

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

$$K_{eq} = \frac{1.30 \times 10^{-4}}{(8.70 \times 10^{-4})(8.70 \times 10^{-4})}$$

$$K_{eq} = 172$$

You will calculate the equilibrium constant for each solution in part B and then determine the average, standard deviation, and relative standard deviation.

Procedure

A. Creating the Calibration Curve

1. Obtain sufficient volume of 0.20 M $Fe(NO_3)_3$ (in 0.1 M HNO_3), 1.0×10^{-3} M NaSCN (in 0.1 M HNO_3), and 0.1 M HNO_3 to make the solutions listed in Table KEQ.1. Record the *exact* concentrations of these two solutions on the Report Sheet.

2. Prepare the set of standard solutions in Table KEQ.1 in separate, clean, labeled 25 mL volumetric flasks using pipets to deliver the volumes of 0.20 M $Fe(NO_3)_3$ and 1.0×10^{-3} M NaSCN. If only one 25 mL volumetric is available, begin with the blank and, once the solution is mixed, transfer it to a large, labeled test tube. Shake any remaining drops of liquid from the volumetric flask into a waste beaker and continue making the solutions in numerical order from 1–5, transferring them to labeled test tubes. If you proceed from a less concentrated to a more concentrated solution of the same reagents, there is no need to wash the volumetric flask between solutions.

Table KEQ.1: Volumes for Standard Solutions

Standard Solution	0.200 M $Fe(NO_3)_3$	1.00×10^{-3} M NaSCN	0.100 M HNO_3
Blank	10.00 mL	0.00 mL	Dilute to 25.00 mL
1	10.00 mL	1.00 mL	Dilute to 25.00 mL
2	10.00 mL	2.00 mL	Dilute to 25.00 mL
3	10.00 mL	3.00 mL	Dilute to 25.00 mL
4	10.00 mL	4.00 mL	Dilute to 25.00 mL
5	10.0 mL	5.00 mL	Dilute to 25.00 mL

3. Turn on the spectrophotometer and set the wavelength to 447 nm.

4. Rinse a cuvette with several portions of the blank solution and then fill it 3/4 full with the blank solution. Holding the cuvette on the cloudy or etched sides, dry to outside of the cuvette with a Kimwipe, making sure to remove any fingerprints from the clear sides.

5. Place the cuvette in the spectrophotometer such that the light path goes through the clear sides and close the lid. Set the readout to 0.00 Absorbance or 100 % Transmittance. Remove the cuvette. Take care not to bump the adjustments or wavelength on the spectrophotometer.

6. Record the absorbance of the standard solutions 1–5 following these steps:
   - Empty of cuvette and rinse it with with several portions of the next solution to be measured.
   - Fill it 3/4 full with a fresh volume of the solution and dry off the outside of the cuvette.
   - Place the cuvette in the spectrophotometer, taking care to place it correctly in the light path and to align any placement marks (if present).
   - Record the absorbance on the Report Sheet.

7. Retain these solutions, especially the blank, until after you have completed part B.

B. Determining the Equilibrium Constant

1. Obtain sufficient volume of 2.00×10^{-3} M $Fe(NO_3)_3$ (in 0.100 M HNO_3), 2.00×10^{-3} M NaSCN (in 0.100 M HNO_3), and 0.100 M HNO_3 to make the solutions listed in Table KEQ.2. Record the *exact* concentrations of these two solutions on the Report Sheet.

   These are **NOT** the same concentrations as the solutions used in part A.

Table KEQ.2: Volumes for the Test Solutions

Test Solution	2.00×10^{-3} M $Fe(NO_3)_3$	2.00×10^{-3} M NaSCN	0.100 M HNO_3)
6	5.00 mL	1.00 mL	4.00 mL
7	5.00 mL	2.00 mL	3.00 mL
8	5.00 mL	3.00 mL	2.00 mL
9	5.00 mL	4.00 mL	1.00 mL
10	5.00 mL	5.00 mL	0.00 mL

2. Prepare the test solutions in Table KEQ.2 in a 10 mL volumetric flask using pipets to deliver the correct volumes of 2.00×10^{-3} M $Fe(NO_3)_3$, 2.00×10^{-3} M NaSCN, and 0.100 M HNO_3. If only one 10 mL volumetric is available, make test solution 6 and, once the solution is mixed, transfer it to a labeled test tube. Shake any remaining drops of liquid from the volumetric flask into a waste beaker and then rinse the volumetric with several small volumes of 0.100 M HNO_3 before making the next solution.

3. Repeat steps 4 and 5 from Part A to clean the cuvette and to recalibrate the spectrophotometer.

4. Record the absorbance of test solutions 6–10 following these steps:

   - Empty of cuvette and rinse it with with several portions of the next solution to be measured.
   - Fill it 3/4 full with a fresh volume of the solution and dry off the outside of the cuvette.
   - Place the cuvette in the spectrophotometer, taking care to place it correctly in the light path and to align any placement marks (if present).
   - Record the absorbance in on the Report Sheet.

5. Dispose of all waste thiocyanatoiron(III) solutions form parts A and B in the appropriately labeled waste container.

Data Analysis

A. Creating the Calibration Curve

1. Calculate the molar concentration of $FeNCS^{2+}$ in standard solutions 1–5, assuming that the reaction has gone to completion and that NaSCN is the limiting reactant in each case.

2. Create an Excel file with two columns: Absorbance and [$FeNCS^{2+}$] and enter your data from part A.

   a. Review the *Excel Basics* video, from timestamp 3:36 to timestamp 4:27. Insert a scatter plot and select the data for the x and y values as shown in the video. Set the [$FeNCS^{2+}$] as the x values and Absorbance as the y values.
   b. Review the *Excel Basics* video from timestamp 4:27 to timestamp 5:35 and format the chart to change the title and to add labels to both axes, following the example in the video.
   c. Review the *Excel Basics* video from timestamp 6:09 to timestamp 7:01 and follow the example to fit your

data to a linear trendline and to display the equation and R-squared value on the chart.

d. Double click on the equation to change the "y" and "x" to "Absorbance" and "[$FeNCS^{2+}$]" respectively.

e. If needed, this page of the workbook can be printed; both the data and the graph will be on one page. Alternatively, by clicking on the graph and then printing, you will obtain a full page chart.

3. Record your slope, intercept and r^2 values for your calibration curve in the report.

B. Determining the Equilibrium Constant

1. Use the calibration curve to determine the equilibrium concentration of [$FeNCS^{2+}$] in each of the test solutions.

2. Create an ICE table for each test solution to determine the equilibrium concentrations of $Fe(NO_3)_3$ and NaSCN.

3. Calculate K_{eq} using the equilibrium concentrations for each test solution and Equation KEQ.5. You will have five values for K_{eq}.

4. Determine the average K_{eq} value, standard deviation and relative standard deviation.

A. Creating the Calibration Curve

Molar concentration of $Fe(NO_3)_3$ _____

Molar concentration of NaSCN _____

Report Table KEQ.1: Absorbance of Standard Solutions

Standard Solution	Absorbance
blank	0.00
Standard solution 1	
Standard solution 2	
Standard solution 3	
Standard solution 4	
Standard solution 5	

B. Determining the Equilibrium Constant

Molar concentration of $Fe(NO_3)_3$ _____

Molar concentration of NaSCN _____

Report Table KEQ.2: Absorbance of Test Solutions

Test Solution	Absorbance
blank	0.00
Test solution 6	
Test solution 7	
Test solution 8	
Test solution 9	
Test solution 10	

Show your work for one example calculation for each of the following:

Equilibrium concentration of $FeSCN^{2+}$.

Equilibrium concentration of $Fe(NO_3)_3$

Equilibrium concentration of NaSCN

Value of K_{eq}