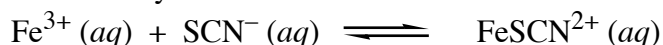# 7

Determination of an Equilibrium Constant

Introduction

When chemical substances react, the reaction typically does not go to completion. Rather, the system goes to some intermediate state in which the rates of the forward and reverse reactions are equal. In this state, the reactants and the products have concentrations which 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 and thiocyanate ion:

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

When solutions containing Fe^{3+} ion and thiocyanate ion are mixed, they react to some extent, forming the $FeSCN^{2+}$ complex ion, which has a deep red color. As a result of the reaction, the equilibrium amounts of Fe^{3+} and SCN^- will be less than they would have been if no reaction had occurred; for every mole of $FeSCN^{2+}$ formed, one mole of Fe^{3+} and one mole of SCN^- will react. The equilibrium constant expression K_c for Reaction 1 is:

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

The value of K_c is constant at a given temperature. This means that mixtures containing Fe^{3+} and SCN^- will come to equilibrium with the same value of K_c, no matter what initial amounts of Fe^{3+} and SCN^- were used. Our purpose in this experiment will be to find K_c for this reaction for several mixtures that have been made up in different ways, and 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 $FeSCN^{2+}$ 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, $Fe(NO_3)_3$, and potassium thiocyanate, KSCN. The color of the $FeSCN^{2+}$ ion formed will allow us to determine its equilibrium concentration. Knowing the initial composition of a mixture and the equilibrium concentration of $FeSCN^{2+}$, we can calculate the equilibrium concentrations of the rest of the pertinent species and then determine K_c.

Method for Determining [$FeSCN^{2+}$]

In this experiment, you will use a spectrophotometer to determine [$FeSCN^{2+}$] in the equilibrium mixtures. Instructions for use of the Spectronic 20D spectophotometer are attached. The spectrophotometer measures <u>absorbance</u>, the amount of light absorbed by the complex at a given wavelength. Beer's law expresses the relationship between absorbance, A, and concentration of a colored species, c.

$$A = \varepsilon bc$$

Here, ε is a constant that depends on the wavelength of light and on the substance that is absorbing the light; b is the distance that the light travels through the sample of the absorbing substance.

The $FeSCN^{2+}$ complex absorbs blue light. That is why it has a reddish orange color. It absorbs the most light at a wavelength of 447 nm. Therefore, at this wavelength absorbance measurements will have the highest sensitivity to [$FeSCN^{2+}$]. In this experiment, you will measure the absorbance of all solutions at 447 nm.

In the <u>first part</u> of the experiment, you will determine the relationship between the absorbance and [$FeSCN^{2+}$] at 447 nm. You will do this by measuring the absorbance of three standard solutions, in which [$FeSCN^{2+}$] is known. There is a problem here: how can known concentrations of $FeSCN^{2+}$ be obtained? $FeSCN^{2+}$ participates in the equilibrium with Fe^{3+} and SCN^- ions. Known amounts of the reactants will not necessarily yield a known amount of the product.

This difficulty can be avoided. According to Le Châtelier's principle, a net reaction from left to right (that is, in the forward direction) occurs when more of a reactant is added. As more and more of the same reactant is added, more and more of the product will be formed. It is possible to add so much of this reactant that essentially all of the other reactant will be converted to product. You will use limiting quantities of SCN^- and overwhelming amounts of Fe^{3+} to produce known amounts of $FeSCN^{2+}$ in your standard solutions. The amount of $FeSCN^{2+}$ that is formed will then be essentially equal to the starting amount of the limiting reactant.

Once you have measured the absorbances of the standard solutions, you will plot the absorbances against the concentrations of $FeSCN^{2+}$ on a graph, or "calibration curve". The points on the calibration curve will fall on a straight line, which has a slope of εb, the constant of proportionality between absorbance and concentration. You can use this calibration curve to find [$FeSCN^{2+}$] in other solutions.

In the <u>second part</u> of the experiment, you will measure the absorbance of a different set of solutions, in which substantial amounts of both reactants and the product are present. You will use your calibration curve to convert the measured absorbance to the equilibrium concentration of $FeSCN^{2+}$ in each solution. From the initial concentrations of the reactants and the equilibrium concentration of the product, you will calculate the equilibrium constant for the reaction.

In preparing each of the mixtures in this experiment you will maintain the concentration of 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 $FeOH^{2+}$, which would interfere with the analysis of $[FeSCN^{2+}]$.

Experimental Procedure

SAFETY PRECAUTIONS: Wear your SAFETY GOGGLES. Nitric acid (HNO_3) is corrosive. If any solutions containing nitric acid splash onto your hands or clothing, wash them off immediately with copious amounts of running water.
WASTE DISPOSAL: All waste from this experiment should be poured into the INORGANIC WASTE containers in the fume hood.

Part 1: Finding the relationship between absorbance and $[FeSCN^{2+}]$

Label 3 medium-sized test tubes. Table 7.1 shows the amounts of the **concentrated 0.20 M** $Fe(NO_3)_3$ (in 1 M HNO_3) solution, 2.00×10^{-3} M KSCN solution, and purified water that should be added to each tube. Pipet the approximate amount of each solution into each tube. (Record the <u>exact</u> amount of each solution that you actually add. You will need to use these actual amounts in your calculations.)

Obtain three separate small pieces of parafilm. Close the top of each test tube with the parafilm. Mix each solution thoroughly by inverting the test tube several times. Record your observations. (How do the colors of the five solutions compare?)

Zero the spectrophotometer. Then, measure and record the absorbance of each solution at 447 nm. Instructions for use of the spectrophotometers are on pages 28-29.

Table 7.1 Composition of solutions for preparing the calibration curve.

Test Tube	Volume of **concentrated 0.20 M** $Fe(NO_3)_3$ in 1 M HNO_3 (mL)	Volume of 2.00×10^{-3} **M** KSCN (mL)	Volume of purified water (mL)
1-1	5.0	0.50	4.5
1-2	5.0	1.0	4.0
1-3	5.0	1.5	3.5

Part 2: Determining the equilibrium constant.

Label 5 medium-sized test tubes. Table 7.2 shows the amounts of 2.00×10^{-3} M $Fe(NO_3)_3$ (in 1 M HNO_3) solution, 2.00×10^{-3} M KSCN solution, and purified water that should be added to each tube. Pipet the approximate amount of each solution into each tube. (Record the <u>exact</u> amount of each solution that you actually add. You will need to use these actual amounts in your calculations.)

Obtain five separate small pieces of parafilm. Close the top of each test tube with the parafilm. Mix each solution thoroughly by inverting the test tube several times. Record your observations.

Measure and record the absorbance of each solution at the 447 nm.

Table 7.2 Composition of solutions for determining the equilibrium constant.

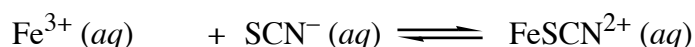| Test Tube	Volume of 2.00×10^{-3} M $Fe(NO_3)_3$ in 1 M HNO_3 (mL)	Volume of 2.00×10^{-3} M KSCN (mL)	Volume of purified water (mL)
2-1	5.0	1.0	4.0
2-2	5.0	2.0	3.0
2-3	5.0	3.0	2.0
2-4	5.0	4.0	1.0
2-5	5.0	5.0	none

Calculations

Part 1. Graphing the relationship between absorbance and [FeSCN^{2+}].

Assuming that "all" of the SCN^- ions have been converted to $FeSCN^{2+}$ ions, calculate [$FeSCN^{2+}$] in each of the solutions in Part 1. For example, in test tube 1-2, 1.0 mL of a 2.00×10^{-3} M KSCN solution was diluted to 10.0 mL. The concentration of SCN^- that results from this dilution is the one to use for determining [$FeSCN^{2+}$]. Because of the 1:1 stoichiometry, that initial concentration of SCN^- is equal to [$FeSCN^{2+}$].

Plot a full-page graph of the absorbance against the concentration of $FeSCN^{2+}$ in all standard solutions. Use a ruler to draw the best straight line that comes closest to each of your five data points. Your line should pass through (0 M, 0). (Why?) This graph is your calibration curve. When you measure the absorbance of a solution that contains an unknown concentration of $FeSCN^{2+}$ ions, you can use this calibration curve to determine the unknown concentration.

Part 2: Determining the equilibrium constant.

Calculate the value of the equilibrium constant for Reaction (1) from your data for each of the five solutions in Part 2. You may find it helpful to organize each of your five calculations in an equilibrium table such as this one:

	Fe^{3+} (aq)	+ SCN^- (aq) $\rightleftharpoons$	$FeSCN^{2+}$ (aq)
Initial concentration (M)			
Change in concentration (M)			
Equilibrium concentration (M)			

The calculations for Part 2 are most easily done by following Steps 1 through 5, which are illustrated in the sample calculations below.

Step 1. Find the *initial* concentrations of Fe^{3+} and SCN^- in the mixtures in test tubes 2-1 through 2-5. You will need to account for dilutions of the stock solutions.

Step 2. Use the measured absorbances of these solutions and your calibration curve to find the *equilibrium* concentration of $[FeSCN^{2+}]$ in these solutions.

Step 3. Find the *change* in concentration of $FeSCN^{2+}$. Deduce the *changes* in concentration of the reactants, Fe^{3+} and SCN^-. The changes in concentration of all three species should be consistent with the stoichiometry of the reaction.

Step 4. Find the *equilibrium* concentrations of the reactants, Fe^{3+} and SCN^-.

Step 5. Calculate K_c for the reaction for each of the mixtures by substituting values for the equilibrium concentrations of Fe^{3+}, SCN^-, and $FeSCN^{2+}$ into the equilibrium constant expression.

Sample Calculations (Part 2): Suppose that we prepare a mixture by mixing 10.0 mL of 2.00×10^{-3} M $Fe(NO_3)_3$ with 10.0 mL of 2.00×10^{-3} M KSCN. Some red $FeSCN^{2+}$ ion is formed by the complexation reaction. Its concentration at equilibrium is found to be 2.50×10^{-4} M. Our problem is to find K_c for the reaction from this information.

Step 1: Find the initial concentrations.

The initial concentrations of the reactants can be found from the following relation:

initial concentration of reactants in mixture

$$= \text{concentration of stock solution} \times \frac{\text{volume of stock solution used}}{\text{total volume of mixture}}$$

initial concentration of Fe^{3+} = 2.00×10^{-3} M $\times \dfrac{0.010 \text{ L}}{0.010 \text{ L} + 0.010 \text{ L}}$ = 1.00×10^{-3} M

initial concentration of SCN^- = 2.00×10^{-3} M $\times \dfrac{0.010 \text{ L}}{0.010 \text{ L} + 0.010 \text{ L}}$ = 1.00×10^{-3} M

initial concentration of $FeSCN^{2+}$ = 0.00 M, because we did not add any to the mixture.

Step 2: Fill in the equilibrium concentration of product.

From our spectrophotometric data, we know that the equilibrium concentration of $FeSCN^{2+}$ is 2.50×10^{-4} M (or 0.250×10^{-3} M).

After completing Steps 1 and 2, the equilibrium table contains the following information:

	Fe^{3+} (aq)	+ SCN⁻ (aq) ⇌	$FeSCN^{2+}$ (aq)
Initial concentration (M)	1.00×10^{-3}	1.00×10^{-3}	0
Change in concentration (M)			
Equilibrium concentration (M)			0.250×10^{-3}

Step 3: Find the change in concentration of each reactant.

Since the concentration of product, $FeSCN^{2+}$, has increased by 2.50×10^{-4} M, the concentrations of the reactants, Fe^{3+} and SCN⁻, must have decreased by the same amount. This is due to the 1:1 stoichiometric ratio; one mole each of Fe^{3+} and SCN⁻ are used up for every one mole of $FeSCN^{2+}$ that is formed.

Step 4: Find the equilibrium concentration of each reactant.

When we know the initial concentrations of the reactants and the changes in those concentrations, we add them to find the equilibrium concentrations.

After completing Steps 3 and 4, the equilibrium table contains the following information:

	Fe^{3+} (aq)	+ SCN⁻ (aq) ⇌	$FeSCN^{2+}$ (aq)
Initial concentration (M)	1.00×10^{-3}	1.00×10^{-3}	0
Change in concentration (M)	-0.250×10^{-3}	-0.250×10^{-3}	$+0.250 \times 10^{-3}$
Equilibrium concentration (M)	0.75×10^{-3}	0.75×10^{-3}	0.250×10^{-3}

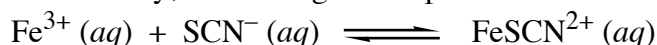Step 5: Find K_c for the reaction.

Once the equilibrium concentrations of all the reactants and products are known, they can be substituted into the equilibrium expression to determine K_c.

$$K_c = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{0.250 \times 10^{-3}}{(0.75 \times 10^{-3}) \times (0.75 \times 10^{-3})} = 4.4 \times 10^2$$

Your experimental result for K_c will be different from this result, because the data in this example were obtained at a different temperature.

Pre-lab Question

A student does an experiment to determine the equilibrium constant for the same reaction that you will study, but at a higher temperature.
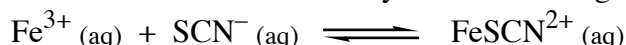
$$Fe^{3+} (aq) + SCN^- (aq) \rightleftharpoons FeSCN^{2+} (aq)$$

The student mixes 5.00 mL of 2.00×10^{-3} M $Fe(NO_3)_3$ solution with 5.00 mL of 2.00×10^{-3} M KSCN solution, heats the mixture, and finds that the equilibrium concentration of $FeSCN^{2+}$ in the mixture is 5.00×10^{-5} M.

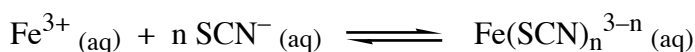Calculate the equilibrium constant for the reaction under the conditions in this experiment.

(Show your work. Answer: $K_c = 55$.)
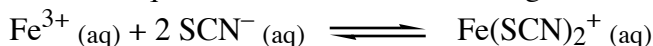

Additional Questions (for the finished lab report)

1. You have been told that the reaction you are observing is:

    $$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons FeSCN^{2+}_{(aq)}$$

    You could have figured this out for yourself from your data, if you knew that the reaction must be of the form:

    $$Fe^{3+}_{(aq)} + n\, SCN^-_{(aq)} \rightleftharpoons Fe(SCN)_n^{3-n}_{(aq)}$$

    (a) Using your data from the mixtures in test tubes 2-1, 2-3, and 2-5, recalculate three new equilibrium constants, assuming that the reaction is:

    $$Fe^{3+}_{(aq)} + 2\, SCN^-_{(aq)} \rightleftharpoons Fe(SCN)_2^+_{(aq)}$$

    Hint: Notice that the *change* in concentration of SCN^- in your equilibrium table will change because of the new stoichiometry. Also, the exponent on $[SCN^-]$ in the equilibrium constant expression will change for the same reason.

    (b) Why do the results of your calculation in (a) show that the reaction you are observing is more likely to be the first one (one mole of SCN^- complexes with one mole of Fe^{3+})?

2. In Part 1 of this experiment, you made the assumption that the $FeSCN^{2+}$ concentrations in your standard solutions were equal to the initial concentrations of SCN^- ions. Now that you know the value of the equilibrium constant, calculate the actual equilibrium concentrations of Fe^{3+}, SCN^-, and $FeSCN^{2+}$ in mixture in test tube 1-2. (How good was the assumption?)

Procedure for use of Spectronic 20D Spectrophotometers

General Technique

Successful use of the spectrophotometer depends on the consistent use of correct laboratory procedures and analytical techniques. To minimize problems, follow these guidelines:

- Keep all solutions free of bubbles.
- Make sure that all sample holders are at least half full.
- Use the same cuvette for both sample and blank measurements.
- Make sure that the mark (fiducial line) on the test tube aligns with the mark on the adapter toward the front of the instrument.
- During extended operation at a fixed wavelength, check from time to time for 100%T drift.
- Use clean test tubes and do no touch the test tubes below the fiducial line.

Flashing Display

A flashing display indicates that the reading is out of range and the 100%T/0 A control must be adjusted. This adjustment controls an optical occluder which regulates the amount of light passing through the sample.

In 100%T mode, a reading greater than 200%T will cause the display to flash.
- If the flashing reading is –1999, turn the 100%T/0A control clockwise until the display operates normally.
- If the flashing reading is +1999, turn the 100%T/0A control counterclockwise until the display operates normally.

In absorbance mode, a reading greater than 2A will cause the display to flash.
- If the flashing reading is –1999, turn the 100%T/0A control counterclockwise until the display operates normally.
- If the flashing reading is +1999, turn the 100%T/0A control clockwise until the display operates normally.

It may require several complete turns of the 100%T control to return to the proper range.

Change in wavelength

It is important to insert the blank and reset the display to 100% or 0.0 A every time the wavelength is changed.

Taking measurements of Transmittance or Absorbance

Tip: The basic steps for taking measurements are highlighted in **bold text** in the following instructions.

1.	**Turn on** the instrument by turning the Power Switch (knob on the left side of instrument) clockwise. Allow the spectrophotometer to warm up for at least 15 minutes to stabilize.
2.	After the warmup period, **set the desired wavelength** with the Wavelength Control Knob.
3.	**Set the filter lever** to the appropriate position for the selected wavelength.
4.	With the mode set to **transmittance, adjust the display** to 0%T with the Zero Control (knob on the front left side of the instrument). Make sure that the sample compartment is empty and the cover is closed.
5.	**Set the display mode** to TRANSMITTANCE or ABSORBANCE by pressing the MODE control key until the appropriate LED is lit.
6.	Fill a clean cell with water (or another blank solution) and wipe the cell with a tissue to remove liquid droplets, dust and fingerprints.
7.	**Place the cell in the sample compartment** and align the guide mark on the cell with the guide mark at the front of the sample compartment. Press the cell firmly into the sample compartment and close the lid.
8.	**Adjust the display to 100%T or 0.0A** with the Transmittance/Absorbance Control (knob on the right side of the instrument).
9.	Remove the cell from the sample compartment and empty the water.
10.	Rinse the cell twice with small volumes of the solution to be measured and fill it with the solution.
11.	Wipe the cell with a tissue and **insert the cell into the sample compartment**. Align the guide marks and close the lid.
12.	**Read the appropriate value (%T or A)** from the display.
13.	Remove the cell from the sample compartment and repeat steps 10 through 12 for any remaining sample solutions.
14.	When all measurements are completed, turn off the spectrophotometer by turning the Power Switch counterclockwise until it clicks.