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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:

$$Fe^{3+}\,(aq) + SCN^{-}\,(aq) \rightleftharpoons FeSCN^{2+}\,(aq) \qquad (1)$$

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.

Reaction mixtures will be prepared by mixing solutions containing known concentrations of iron (III), or $Fe(NO_3)_3$, and thiocyanate ion, or KSCN. The.

absorbance of blue light at λ=447nm) of the product ion $FeSCN^{2+}$ allows determination of [$FeSCN^{2+}$] at equilibrium. Knowing the initial concentrations of reactants and the measured equilibrium molarity of $FeSCN^{2+}$, you can complete the Initial-Change-Equilibrium (ICE) table and determine K_c as we have done in several example and homework problems.

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

We use a spectrophotometer to determine [$FeSCN^{2+}$] in the equilibrium mixtures. Instructions for use of the Spectronic 20D spectrophotometer are attached. The spectrophotometer measures absorbance, the amount of light absorbed by the complex at a given wavelength. Beer's Law expresses the relationship between absorbance and concentration of some colored species, c.

$$\text{Abs} = \varepsilon bc$$

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.

In our case, Beer's Law simplifies to:

$$\text{Abs(447nm)} = \text{constant x } [FeSCN^{2+}]$$

where you will determine the constant experimentally by plotting absorbance at 447 nm "A" or "Abs" vs an assumed known [$FeSCN^{2+}$]. This plot is called a "calibration curve" and will be used to determine unknown concentrations [$FeSCN^{2+}$] in the Part 2 of the experiment.

The $FeSCN^{2+}$ complex ion absorbs blue light which is why it appears reddish orange. 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.

Your job in Part I is to plot absorbance at 447 nm against known [$FeSCN^{2+}$] to generate a calibration curve. You will do this by measuring the absorbance of three standard solutions, in which [$FeSCN^{2+}$] is assumed to be known. There is a problem here: How can we know [$FeSCN^{2+}$] ahead of time if we don't know Kc to begin with?

The trick is to swamp the system with Fe^{3+} and assume the SCN^{-} is then used up as a limiting reactant. It is possible to add so much of this reactant that essentially all of the other reactant will be converted to product (LeChatler's Principle). You will use limiting quantities of SCN^{-} and overwhelming amounts of Fe^{3+} to produce known amounts of $FeSCN^{2+}$ in your standard solutions: From reaction stoichiometry the amount of $FeSCN^{2+}$ formed will nearly equal the starting amount of the limiting reactant SCN^{-}.

To reiterate, once you have measured the absorbances of the three 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 should fall on a straight line, with slope εb, the constant of proportionality between absorbance and [$FeSCN^{2+}$]. The calibration curve is then used to find unkonwn [$FeSCN^{2+}$] in Part 2.

In Part 2, you will measure Abs(447nm) in solutions (not swamped with Fe^{3+}) for which substantial amounts of reactants and product are present! Your calibration curve from Part I allows you to determine [$FeSCN^{2+}$] from the measured absorbance. From the initial concentrations of the reactants and the equilibrium concentration of the product, you will complete the familiar "Initial-Change-Equilibrium" table and calculate Kc.

(In these reaction mixtures the concentration of H^+ is maintained at 0.5 M with nitric acid. H^+does not participate in the reaction but is necessary to prevent brown-colored species like $FeOH^{2+}$, which interfere with 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 three 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. **Use Gilson pipetmen to deliver the correct volumes of reactant solutions and water. Get your lab instructor or laboratory technician to show you how to use and calibrate the delivery volume of a Gilson pipetman.**

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?)

Make sure the spectrometer is on the "absorbance" readout setting and that it reads zero absorbance when your cuvette is contains pure water. You will use a single cuvette for all absorbance measurements! Why? After you are sure the spectrometer is zeroed (get help for this if it is not) measure and record the absorbance for each solution (at 447 nm) using the same cuvette. 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 five medium-sized test tubes. Table 7.2 shows the amounts of the dilute **2.00×10^{-3} M** $Fe(NO_3)_3$ (in 1 M HNO_3) solution, the 2.00×10^{-3} M KSCN solution, and the purified water that should be added to each tube. Again, use the appropriate calibrated Gilson pipetman to deliver the necessary volumes.

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.

With the same cuvette as you used in Part I, 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. Creating a calibration curve by graphing absorbance vs [$FeSCN^{2+}$].

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 assumed to be equal to [$FeSCN^{2+}$].

Plot a full-page graph of the absorbance against [$FeSCN^{2+}$] for your three standard solutions. Use a ruler or the Microsoft Excel linear regression tool to draw the best straight line through your three data points and (0,0). Your line should pass through (A=0.00, [$FeSCN^{2+}$]=0.00 M). Why? This graph is your calibration curve. In Part 2 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 from the measured absorbance.

Part 2: Determining the equilibrium constant.

For each of the five solutions in Part 2, calculate the value of the equilibrium constant for Reaction (1). 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 molarity (M)			
Change in molarity (M)			
Equilibrium molarity (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.

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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

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

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

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

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*) $\rightleftharpoons$	$FeSCN^{2+}$ (*aq*)
Initial molarity (M)	1.00×10^{-3}	1.00×10^{-3}	0
Change in molarity (M)			
Equilibrium molarity (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*) $\rightleftharpoons$	$FeSCN^{2+}$ (*aq*)
Initial molarity (M)	1.00×10^{-3}	1.00×10^{-3}	0
Change in molarity (M)	-0.250×10^{-3}	-0.250×10^{-3}	$+0.250 \times 10^{-3}$
Equilibrium molarity (M)	0.75×10^{-3}	0.75×10^{-3}	0.250×10^{-3}

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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.

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 (Use Absorbance here!)

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.