Experiment 19

FV 2/5/01

SPECTROPHOTOMETRIC DETERMINATION OF AN EQUILIBRIUM CONSTANT

MATERIALS: Spectronic 20, cuvette, two 50 mL beakers, 5 mL volumetric pipet, two plastic Pasteur pipets, 10 mL graduated cylinder, 25.00 mL volumetric flask, 0.20 M $Fe(NO_3)_3$ solution in 0.5 M HNO_3, 5.00 x 10^{-4} M KSCN solution in 0.5 M HNO_3, 0.50 M HNO_3 in 50:50 acetone/water, small weighing boat.

PURPOSE: The purpose of this experiment is to determine the equilibrium constant for the reaction between Fe^{3+} and SCN^- to produce $Fe(SCN)^{2+}$.

LEARNING OBJECTIVE: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Use a Spectronic 20 spectrometer to measure percent transmittance of a solution.
2. Calibrate a Pasteur pipet to deliver small volumes of a reactant.
3. Derive an equation relating an equilibrium constant of a reaction to experimentally measured variables.
4. Determine the equilibrium constant for the formation of the thiocyanatoiron(III) complex.

DISCUSSION:

Review Appendix I for a discussion of spectroscopy and Beer's Law.

In aqueous solution, iron(III) ions, Fe^{3+}, react with thiocyanate ions, SCN^-, to form the thiocyanatoiron(III) complex ion, $Fe(SCN)^{2+}$. The reaction is an equilibrium process and does NOT go to completion. It may be represented by the net ionic equilibrium equation

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

and the associated equilibrium constant expression is:

$$K = \frac{[Fe(SCN)^{2+}]_{(eq)}}{[Fe^{3+}]_{(eq)}[SCN^-]_{(eq)}} \qquad (1)$$

where the concentrations of all species refer to equilibrium concentrations.

One way to determine K for such a reaction is to mix solutions having known concentrations of iron(III) and thiocyanate ions. When equilibrium is reached, the unknown concentration of the product, thiocyanatoiron(III) complex, can be represented as x (in mol/L). The value for the equilibrium constant would then be found from simple stoichiometric considerations, which are often shown in an "ICE table".

	Fe^{3+} (aq)	+	SCN^- (aq)	$\rightleftharpoons$	$Fe(SCN)^{2+}$ (aq)
Initial concentration	$[Fe^{3+}]_0$		$[SCN^-]_0$		0
Change in concentration	$-x$		$-x$		x
Equilibrium concentration	$[Fe^{3+}]_0 - x$		$[SCN^-]_0 - x$		x

$$K = \frac{x}{([Fe^{3+}]_0 - x)\cdot([SCN^-]_0 - x)} \tag{2}$$

The difficulty lies in determining the concentration of the complex, x. Of the three species present (Fe^{3+}, SCN^-, and $Fe(SCN)^{2+}$), only the complex $Fe(SCN)^{2+}$ absorbs visible light. The thiocyanatoiron(III) complex, $Fe(SCN)^{2+}$, is blood red in color due to the absorption of blue light, with a maximum absorption at 450 nm. Hence, it would seem possible to take advantage of this to determine the needed information, since the Beer-Lambert law states that concentration and absorbance are directly related, $A = \varepsilon lc$. Applying Beer's Law to the measured absorbance of the equilibrium solution would yield the concentration of the complex, x. This could be substituted into the ICE table to find the value of K. The problem with this direct approach is that the value of the molar absorptivity, ε, is not known. Without knowing ε for this particular complex, none of the desired concentrations can be determined.

In this experiment, an alternative approach will be used. The equilibrium constant, K, *and* the molar absorptivity, ε, will be determined *simultaneously*. To understand how this approach works, consider the expression for the equilibrium constant, equation (2). The experiment will be run with a large excess of iron(III) ions and therefore ($[Fe^{3+}]_0 - x$) is approximately equal to $[Fe^{3+}]_0$. According to Beer's Law, $x = A/\varepsilon l$, where $x = [Fe(SCN)^{2+}]$. (The pathlength of the cuvettes used in this experiment is one cm, $l = 1$.) Substitution of the relationship $x = A/\varepsilon l$ into equation (2) above and additional algebraic manipulation produces the following equation:

$$\frac{1}{[Fe^{3+}]_0} = K\cdot\varepsilon\cdot\ell\cdot\left(\frac{[SCN^-]_0}{A}\right) - K \tag{3}$$

This equation shows that if a set of mixtures is prepared with varying initial iron(III) concentrations (with Fe^{3+} always kept in excess), measuring the absorbances, A, of these solutions would lead to the necessary data to determine K and ε. A plot of $1/[Fe^{3+}]_0$ *vs.* $[SCN^-]_0/A$ will give a straight line with a slope equal to $K\cdot\varepsilon\cdot l$ and a y-intercept equal to $-K$. In this manner, both the equilibrium constant, K, of the reaction and the molar absorptivity, ε, of the complex can be determined from this plot.

PROCEDURE:

Part A. Calibration of the Pasteur Pipet

1. Obtain a clean plastic Pasteur pipet, a beaker and a 10.0 mL graduated cylinder.

2. Place approximately 10 mL of the iron(III) nitrate solution in the beaker. Use the plastic Pasteur pipet to transfer 5.0 mL of this solution to the graduated cylinder. Be sure to adjust the bottom of the meniscus to the mark.

3. Hold the Pasteur pipet vertically and add additional iron(III) nitrate solution in uniform drops, counting the number of drops until the meniscus rises to the 6.0 mL mark. In the Data Section, record the number of drops added.

4. Repeat this process, adding an additional 1.0 mL to the graduated cylinder. Record the number of drops for the second trial. This calibrated pipet will be used to add the iron(III) nitrate solution in Part B. Save the solution and pipet for Part B.

Part B. Equilibrium Measurements

1. Prepare a dilute potassium thiocyanate solution as follows. Rinse a 5 mL volumetric pipet with a small portion of the 5.00×10^{-4} M potassium thiocyanate solution and discard the rinses. With the pipet, transfer 5.00 mL of the 5.00×10^{-4} M potassium thiocyanate solution to the 25.00 mL volumetric flask. Dilute to the mark with the supplied 0.5 M HNO_3 in water/acetone solvent. Mix the solution well by inverting the capped volumetric flask. Clean the pipet with distilled water.

2. Transfer about 10 mL of the dilute potassium thiocyanate solution to a clean, dry 50 mL beaker. Use this to rinse the volumetric pipet. Using this rinsed pipet, transfer exactly 5.00 mL of the dilute potassium thiocyanate solution from the **volumetric flask** into the cuvette.

3. Set the wavelength of the Spectronic 20 to 450 nm. Adjust the zero and 100% transmittance settings on the Spectronic 20, using the dilute thiocyanate solution as the blank.

4. Using the calibrated Pasteur pipet, draw up some of the iron(III) nitrate solution from the graduated cylinder from Part A. Release a drop to get rid of any air bubbles, holding the pressure with your fingers. Carefully add one *uniform* drop to the solution in the cuvette making sure to hold the pipet vertically. Use a <u>different</u> Pasteur pipet to mix the contents of the cuvette by drawing some of the liquid into the pipet and then expelling it back into the cuvette. Mix the solution well. Be sure not to lose any liquid.

5. Properly insert the cuvette into the Spectronic 20 and record the percent transmittance of the sample.

6. Repeat this process of adding drops and reading percent transmittance, adding one additional drop each time and mixing the solution well before taking the %T measurement. Add a total of nine drops.

7. Wash the cuvette with distilled water. Rinse the cuvette twice with the 0.5 M HNO_3 in water/acetone solvent.

8. Beginning at Step 4, do a second trial with a fresh 5.00 mL sample of dilute potassium thiocyanate solution.

Clean up:

1. Discard all solutions in the sink. Wash all glassware.

2. Return all equipment to their proper locations.

Name_____ Section _____

Partner _____ Date _____

DATA SECTION
Experiment 19

BE SURE TO INCLUDE THE APPROPRIATE UNITS AND SIGNIFICANT FIGURES FOR ALL MEASUREMENTS

Part A. Calibration of the Pasteur Pipet

Drops of solution in 1.0 mL Trial 1: _____

Trial 2: _____

Part B. Equilibrium Data

# of drops of $Fe(NO_3)_3$ solution	% Transmittance	
	Trial 1	Trial 2
0		
1		
2		
3		
4		
5		
6		
7		
8		
9		

DATA TREATMENT
Experiment 19

Part A. Calibration of the Pasteur Pipet

(A.1) Calculate the average number of drops of iron(III) nitrate solution per mL.

Average number of drops per mL $Fe(NO_3)_3$ = drops/mL

Part B. Equilibrium Measurements

(B.1) Calculate the concentration of the dilute potassium thiocyanate solution. Show your work.

Carry out the following for each of the trials.

(B.2) Using a spreadsheet program, enter the values for the concentration of the dilute potassium thiocyanate, the concentration of the iron(III) nitrate solution, and the percent transmittance values. Calculate the following for each solution (0 to 9 drops):

a. Volume of iron(III) nitrate added.
b. Total volume of solution in the cuvette.
c. Concentration of iron(III) ions in the cuvette, which is the initial concentration, $[Fe^{3+}]_0$.
d. Concentration of thiocyanate ions in the cuvette, which is the initial concentration, $[SCN^-]_0$.
e. Absorbance of each solution, A.
f. $1/[Fe^{3+}]_0$.
g. $[SCN^-]_0/A$

(B.3) Construct a graph of $1/[Fe^{3+}]_0$ *vs*. $[SCN^-]_0/A$.

(B.4) Perform a linear regression on the $1/[Fe^{3+}]_0$ *vs*. $[SCN^-]_0/A$ data. Include the regression line, equation of the line, and R^2 value on the graph. Turn in the spreadsheet and graph with your lab report.

(B.5) Using equation (3) and the regression output, determine the values for the equilibrium constant, K, and molar absorptivity, ε. Include the units for ε.

Trial 1:

K = _____ ε = _____

Trial 2:

K = _____ ε = _____

(B.6) Calculate the average values of K and ε.

K = _____ ε = _____

(B.7) For the solution prepared by adding *two* drops of iron(III) nitrate, construct an ICE table (similar to that found on page E19-1). Use your absorbance data to calculate the *equilibrium* concentration of the thiocyanatoiron(III) complex, then determine the *equilibrium* concentrations of the iron(III) ions and thiocyanate ions. Show your work.

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

$[Fe^{3+}]_{eq}$ = _____ $[SCN^{-}]_{eq}$ = _____ $[Fe(SCN)^{2+}]_{eq}$ = _____

(B.8) Using the equilibrium concentrations calculated in (B.7), calculate K for this solution.

K = _____

(B.9) For the solution prepared by adding *six* drops of iron(III) nitrate, construct an ICE table. Use your absorbance data to calculate the *equilibrium* concentration of the thiocyanatoiron(III) complex, then determine the *equilibrium* concentrations of the iron(III) and thiocyanate ions.

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

$[Fe^{3+}]_{eq}$ = _____ $[SCN^{-}]_{eq}$ = _____ $[Fe(SCN)^{2+}]_{eq}$ = _____

(B.10) Using the equilibrium concentrations calculated in (B.9), calculate K for this solution.

K = _____

QUESTIONS
Experiment 19

1. Why are the values of K about the same for each solution? Remember that the solutions contain different initial amounts of the two reagents after each addition of a drop of $Fe(NO_3)_3$ solution.

2. What are the possible experimental sources of error in this experiment? Excluding midshipman and instrument error, list at least three.

3. Comment on the calibration of the Pasteur pipet. Why is this necessary?

Name _____ Section _____

Date _____

PRE-LAB EXERCISES
Experiment 19

1. The percent transmittance values of $Fe(NO_3)_3$ and KSCN are not measured by the Spectronic 20 while that of $Fe(SCN)^{2+}$ is measured. Why?

2. Write out the expression for Beer's law. Rearrange the equation to show how the concentration of the absorbing species, in this case $Fe(SCN)^{2+}$, can be determined from the absorbance.

$[Fe(SCN)^{2+}] = x =$

3. Beginning with equation (2) from page E19-2 and your answer to question 2 above, show the derivation of equation (3) on page E19-2. Remember that the concentration of the complex, x, is much smaller than $[Fe^{3+}]_0$ so that $[Fe^{3+}]_0 >> [Fe(SCN)^{2+}]$.