

Experiment

THE FORMATION CONSTANT FOR A COMPLEX ION BY COLORIMETRY

The CCLI Initiative

Computers in Chemistry Laboratory Instruction

LEARNING OBJECTIVES

The objectives of this experiment are to . . .

- illustrate how colorimetric measurements are made using the *MicroLAB* interface.
- use Beer's Law to measure the equilibrium concentration of a complex ion.
- calculate the equilibrium constant for the formation of a complex ion.

BACKGROUND

Equilibrium

When substances react, the concentrations of reactants and products change continuously until the system reaches chemical equilibrium. At equilibrium, no changes occur in the concentrations of any reactants or products as a function of time, as long as the system is not disturbed.

Equilibrium occurs because chemical reactions are reversible. To illustrate this concept, consider the very important chemical reaction for the synthesis of ammonia from nitrogen and hydrogen:



The double arrows in this equation indicate that $\text{N}_{2(\text{g})}$ and $\text{H}_{2(\text{g})}$ not only can react to form $\text{NH}_{3(\text{g})}$, but that $\text{NH}_{3(\text{g})}$ can decompose to form $\text{N}_{2(\text{g})}$ and $\text{H}_{2(\text{g})}$. When $\text{N}_{2(\text{g})}$ and $\text{H}_{2(\text{g})}$ react in a closed container, the concentrations of these gases will initially decrease, and the concentration of $\text{NH}_{3(\text{g})}$ will increase. As the concentrations of $\text{N}_{2(\text{g})}$ and $\text{H}_{2(\text{g})}$ decrease, fewer $\text{N}_{2(\text{g})}$ and $\text{H}_{2(\text{g})}$ collisions occur, so that the forward reaction will slow down. At the same time, the increase in $\text{NH}_{3(\text{g})}$ concentration results in more $\text{NH}_{3(\text{g})}$ and $\text{NH}_{3(\text{g})}$ collisions and the reverse reaction speed increases. Eventually the forward and reverse rates become equal, and no further changes occur in the concentrations of either reactants or products.

The equilibrium constant

One of the most striking properties of equilibrium is its consistency. For example, at equilibrium the concentrations of the substances in the ammonia synthesis reaction always obey the expression

$$K = \frac{[\text{NH}_3]}{[\text{N}_2][\text{H}_2]^2} \quad (2)$$

where the square brackets indicate equilibrium concentrations in moles/liter. The equilibrium constant, K , is a constant for this reaction at a particular temperature. For example, at 500 C, the measured value of K

is $6.0 \times 10^{-2} \text{ L}^2/\text{mol}^2$, which means that for this reaction system at 500°C equilibrium will be achieved when the concentrations are such that

$$\frac{[\text{NH}_3]}{[\text{N}_2][\text{H}_2]^2} = 6.0 \times 10^{-2} \quad (3)$$

For a general reaction



the equilibrium expression is written

$$K = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \quad (5)$$

where the bracketed capital letters represent concentrations of chemical species and the small letters represent the coefficients in the balanced equation.

In this experiment you will study an equilibrium involving the formation of a complex ion, a species consisting of a metal ion with **ligands** attached to it. A **ligand** is a molecule or ion that has an electron pair that can be used to bond to an empty orbital on the metal ion.

The reaction to be studied in this experiment involves Fe^{3+} and HSCN (thiocyanic acid) reacting to form the orange-red complex ion, FeSCN^{2+} :



The main objective of this experiment is to determine the value of the equilibrium constant (also called the formation constant, K_f , for this reaction). The form of the equilibrium constant expression is given in Equation (7)

$$K_f = \frac{[\text{H}^{+}][\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{HSCN}]} \quad (7)$$

The procedure for determining this formation constant consists of the following steps:

1. Measured volumes of standard $\text{Fe}(\text{NO}_3)_3$ and HSCN solutions in 0.50 M HNO_3 are combined. Simple dilution calculations are used to determine the *initial* molar concentrations of Fe^{3+} and HSCN in the standard solutions.
2. The complex formation reaction is fast and rapidly reaches chemical equilibrium. Colorimetry and Beer's Law, ($A = \epsilon bc$), can be used to determine the molar absorptivity constant of the FeSCN^{2+} complex.
3. The computer's colorimeter works by reading the current of a photomultiplier across the cell from the light source. Thus the light falling on the photomultiplier has passed through the sample being measured, and the current indicates how much light is transmitted by the sample. We convert this current (I) to the absorbance of the solution using the equation $A = \log(I_0/I_t)$, where I_0 is the current of the blank solution and I_t is the current of a specific solution containing the complex ion.

The molar absorptivity constant can be calculated from Beer's Law, using the measured absorbance, the cell path length, b (in cm), and the concentration of FeSCN^{2+} . Under the concentration conditions used for the standard solutions, it can be assumed that all of the HSCN is converted to FeSCN^{2+} .

A plot of absorbance vs. concentration of FeSCN^{2+} in the standard solutions will allow determination of a value of K_f for FeSCN^{2+} at the wavelength emitted by the light emitting diode (the light source). Use the blue light setting of 472 nm on the colorimeter.

- To calculate the formation constant of this complex, you need to determine equilibrium concentrations for all four species involved in the reaction using a second set of solutions. The FeSCN^{2+} concentration in these solutions can be determined by measuring the absorbance of each solution. The equilibrium Fe^{3+} concentration equals its initial concentration minus the equilibrium FeSCN^{2+} concentration. Similarly, the equilibrium HSCN concentration equals its initial concentration minus the equilibrium FeSCN^{2+} concentration. The value of K_f is then calculated by substituting the equilibrium concentrations into Equation (2).
- Five separate determinations of K_f will be made using the procedure just described. This should demonstrate that K_f is a constant; i.e., its value is independent of the initial concentrations used.

THE *MicroLAB* COLORIMETER

Colorimetry is an instrumental method based on the measurement of light absorption by colored solutions and is widely used for performing chemical analyses. The *MicroLAB* model 402 colorimeter utilizes 10 Light Emitting Diodes (LEDs) ranging from 400 to 644 nanometers, spaced about 35 nanometers apart. They are scanned sequentially and the transmittance or absorbance data is presented as 10 colored bars in a bar graph as shown in Figure 1.

These components are arranged such that light from each LED pass through the chromophore (colored substance) solution and falls on a photocell. The photocell circuit produces a current in microamps (I) which is proportional to the light intensity striking the photocell surface and is converted into **Transmittance** and **Absorbance** by the *MicroLAB* software. These components are all housed in the colorimeter chamber of the *MicroLAB* interface.

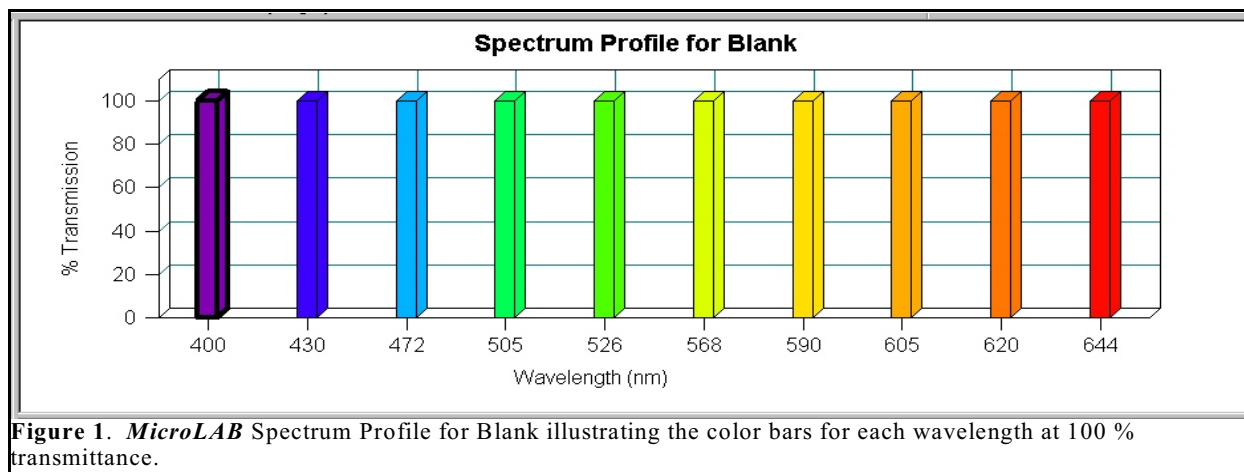


Figure 1. *MicroLAB* Spectrum Profile for Blank illustrating the color bars for each wavelength at 100 % transmittance.

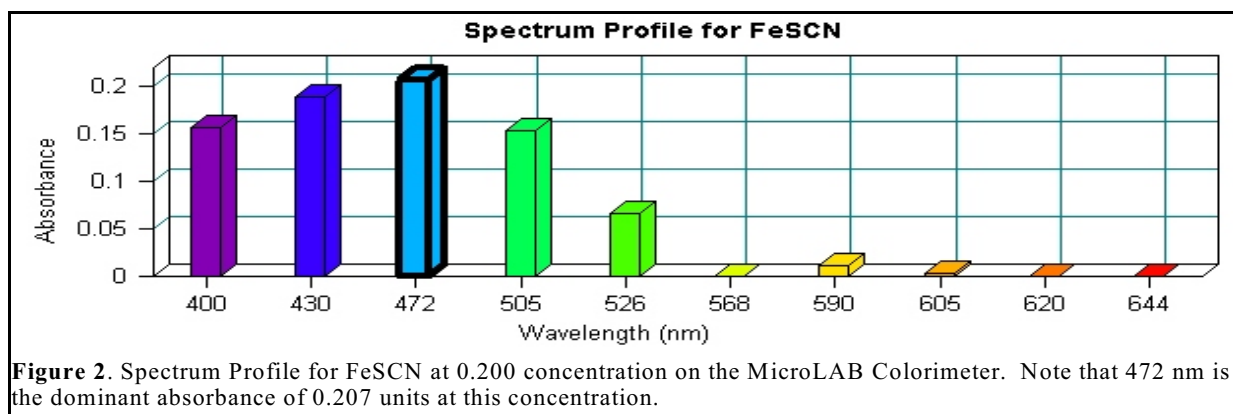
The *MicroLAB* Colorimeter Spectral Profile for the FeSCN at dilute solutions is illustrated in Figure 2.

SAFETY PRECAUTIONS

If skin contact occurs with any solutions, wash the affected area thoroughly with soap and water. Clean up all spills immediately using damp paper towels. At the end of the experiment, all solutions should be discarded into the waste container provided. As always, safety goggles must be worn at all times in the laboratory.

BEFORE PERFORMING THIS EXPERIMENT . . .

...you will need the *MicroLAB Colorimeter* program, which will collect colorimetric data (photocell current vs. concentration).



EXPERIMENTAL PROCEDURE

Preparation of standard solutions

Stock solutions of 0.50 M HNO₃, 0.200 M Fe(NO₃)₃ in 0.50 M HNO₃ and 6.0 x 10⁻⁴ M HSCN in 0.50 M HNO₃ are provided for solution preparation. (Note that there are two different Fe(NO₃)₃ solutions and two different HSCN solutions in the lab. Be sure you use the right ones in each instance.) Using pipets and volumetric flasks *carefully* prepare Solution #1. Work with one solution at a time (see 4. below). You will need to calculate the initial HSCN. This can be accomplished in the **Hand Enter** mode for the spreadsheet and using the **Add Formula** function to make the calculations, then “click-drag them to adjacent columns. (#1 is done for you as a check) **DO THIS BEFORE YOU COME TO LAB!**

Table for Preparing Solutions

	# 1	# 2	# 3	# 4	# 5
mL Fe(NO ₃) ₃	5.00	5.00	5.00	5.00	5.00
ml HSCN	1.00	2.00	3.00	4.00	5.00
ml HNO ₃	4.00	3.00	2.00	1.00	0.00
Total ml	10.00	10.00	10.00	10.00	10.00
Initial [HSCN]	1.00 x 10 ⁻³ M				
Initial [Fe ³⁺]	2.00 x 10 ⁻⁴ M				

Measurements

1. Open the MicroLAB **Colorimeter Experiment** program from the opening screen to do this experiment.
2. Your first sample should be a 0.50 M HNO₃ blank. Fill the cell to about 3/4 full, wipe the clear faces with a Kimwipe, place a mark near the top of the vial and insert the vial into the colorimeter with the mark facing straight forward, then place the cap to prevent stray light from entering. Always mark your vials and set the mark to the front for best results.
3. Measure the **Transmittance** for each of your five prepared solutions, one at a time. You should prepare standard solution #1 and measure its **Transmittance** immediately after preparation since the reading is not stable. After measuring the **Transmittance**, discard the solution. Be sure that each solution is thoroughly mixed before it is used and the cell is carefully dried with a Kimwipe before it is filled. The program will ask for a concentration with each measurement. You should enter the calculated HSCN concentration computed for each of the five solutions (for example, 2.00 x 10⁻⁴ M for HSCN #1) as it is called for in the **Colorimeter** program. This will identify the solution for the Beer's Law plot.

EQUILIBRIUM MEASUREMENTS

Solution preparations

Stock solutions of 0.50 M HNO_3 , $2.00\text{ M Fe(NO}_3)_3$ in 0.50 M HNO_3 and $2.0 \times 10^{-3}\text{ M HSCN}$ in 0.50 M HNO_3 are provided. Again, be sure you are using the correct stock solutions. Initially, prepare only solution #1 in a small beaker using Mohr pipets or pipettors. You will need to input the initial concentrations of HSCN for each of the solutions in this part of the experiment

Although you will need both the initial concentrations of HSCN and Fe^{3+} for your K_f calculations, you will enter only the initial HSCN concentration when using MicroLAB to measure the **Transmittance**.

Measurements

1. Open the *MicroLAB Colorimeter Experiment*.
2. Your first sample should be a 0.50 M HNO_3 blank. Fill the vial about three-fourths full of the blank, insert into the chamber, place the cap, and click on **Blank**.
3. Prepare solution #1 and measure its **Transmittance** immediately. Discard the solution, rinse the cuvette and continue measuring the **Transmittance** for each of the other solutions as you did in the first half of the experiment. Again, the program will ask for a concentration with each measurement. You should enter the initial HSCN concentrations for each of the five solutions.

DATA ANALYSIS

For each experimental solution, do the following:

1. For your first set of data, from the graph of absorbance versus concentration at the maximum absorbance, determine the molar absorptivity constant (ϵ) for FeSCN^{2+} from the slope of the line.
2. Click several other wavelengths and see how the absorptivity constant changes.
3. **Hand Enter** the five **Absorbance** values from your Beer's Law data into the *MicroLAB Experiment Spreadsheet* with Absorbance in Column A and initial [HSCN] in Column B. Using the **Add Formula** function, calculate the equilibrium concentration of the complex ion FeSCN^{2+} in each of the five solutions. This is achieved by dividing absorbance by path length times molar absorptivity (which you determined in the first half of the experiment). "Click-drag" this formula to Column C.
4. Again using the **Add Formula** function, calculate the formation constant (K_f). You should be able to enter a single formula containing the initial Fe^{3+} concentration (this should be the same for all five solutions and should be about 0.00100, use the label value on the container) and data from Columns A and C. "Click-drag" this formula to Column D. You should have five separate values of K_f in Column D.
5. After you have obtained approval of your K_f results from your instructor, print your spreadsheet by **Right Clicking** on the graph and selecting **Print**.
6. Obtain the average value and standard deviation for K_f by **Right Clicking** on the K_f column and clicking on **Column Statistics** and print this window.

