Determining an Equilibrium Constant

INTRODUCTION: In this experiment an equilibrium constant for the formation of a complex ion will be determined. In addition, experience will be gained in the use of the spectrophotometer and Beer's Law.

Iron(III) ions and thiocyanate ions combine in aqueous solution to form a complex ion, thiocyanatoiron(III) ion:

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

The equilibrium constant for this reaction is given by applying the law of mass action:

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

where the square brackets signify equilibrium concentrations. Measurement of these concentrations will enable one to calculate the equilibrium constant.

As you observed in the previous experiment, the product complex ion is the only one of the three species which has an appreciable color (blood-red); therefore, spectrophotometry will be used to measure the concentration of this species. Suppose that a monochromatic (single-wavelength) light beam of intensity **I_o** is directed upon a sample of a light-absorbing (colored) species. A portion of this light is absorbed by the sample and the emerging light beam has a lower intensity **I**. The **transmittanceT** of the sample is defined as follows:

$$T = I/I_o \quad \text{or} \quad \%T = I/I_o \times 100\% \qquad (3)$$

The **absorbance A** of a sample is defined as follows:

$$A = -\log_{10}(T) = \log(I_o/I) = 2 - \log(\%T) \qquad (4)$$

Beer's Law states that absorbance is directly proportional to the molar concentration of an absorbing species:

$$A = ebc \qquad (5)$$

where c stands for molar concentration (molarity), b is the path length of the light through the solution (1.27 cm), and e(epsilon) is a constant (units: L/mol cm) called the molar absorptivity or molar extinction coefficient, which depends upon the nature of the absorbing species, the wavelength, and the temperature. If eand b are known, measurement of the absorbance of a solution enables one to calculate the concentration. Since eand b are constant during an experiment, a plot of absorbance versus molarity will have a slope of **eb**.

Read the description of the use of the Spectronic 20 spectrophotometer from the NT Curriculum Project. In order to view the videos you will need to install the Apple Quicktime program if your computer does not have it installed.

Part I of this experiment involves the preparation of a Beer's Law calibration plot for the $FeSCN^{2+}$ complex ion. Five solutions containing known concentrations of the complex ion will be prepared and their absorbance measured. A plot of absorbance versus concentration will allow calculation of the extinction coefficient. This value may then be used in conjunction with the absorbance of any solution containing the ion to determine its concentration, i.e., once the calibration is made, the absorbance of any solution is divided by the product of the extinction coefficient and the path length to obtain the molarity. The goal of this section of the experiment is to determine the values of the slope and the extinction coefficient.

A problem arises in determining the concentrations of the complex ion to use in the Beer's Law plot. Since the reaction forming the ion is an equilibrium process, it does not proceed to completion; solutions of the complex ion will generally also contain measurable concentrations of the two reactant ions, and the concentration of the complex ion will not be known. However, we can make use of Le Chatelier's Principle (see Experiment 5) to overcome this obstacle. If a limited quantity of iron(III) ion is combined with a large excess of thiocyanate ion, the equilibrium will be shifted far to the product side, essentially to completion. The number of moles of the complex ion formed will then be essentially equal to the number of moles of iron(III) ion that were used initially. A series of five different dilutions of the iron(III) ion will be used to prepare solutions of the complex ion in accord with this principle and a Beer's Law plot will be made in order to determine the extinction coefficient of the complex ion.

Part II of the experiment involves the preparation of the complex ion under true equilibrium conditions using several different sets of initial concentrations. The molarity of the complex ion will then be calculated using the absorbance of the solutions and the results of Part I. The equilibrium concentrations of the other two ions can then be determined through mass balance considerations (stoichiometry).

The calculations in this experiment are somewhat involved and will be illustrated by the following example. In the equilibrium

$$A + B \rightleftharpoons C$$

the equilibrium concentrations of all three species are required in order to calculate K_c. The initial volumes and molarities of A and B are known; these molarities are **not** the same as those existing after equilibrium is attained. The method of analysis used in the experiment provides the molarity of C at equilibrium. The numbers of **moles** of A and B at equilibrium are determined through stoichiometry calculations. In converting back to molarity, the **total combined volume** must be considered.

In the example, 10.0-mL portions of 2.10×10^{-3} M solutions of A and B are combined and allowed to reach equilibrium. Analysis of the mixture reveals that the concentration of C at equilibrium is 1.50×10^{-4} M.

The initial numbers of **moles** of A and B are required in order to do the stoichiometry calculations. Using milliliters and millimoles:

$$(10.0 \text{ mL})(2.10 \times 10^{-3} \text{ mmol/mL}) = 2.10 \times 10^{-2} \text{ mmol A}$$

The calculation is identical for B. For the product C, note that the volume is the total combined volume:

$$(20.0 \text{ mL})(1.50 \times 10^{-4} \text{ mmol/mL}) = 3.00 \times 10^{-3} \text{ mmol C}$$

Now consider the stoichiometry. Each mole of C formed requires that one mole of A and one mole of B be consumed. Thus, the amounts of both A and B remaining at equilibrium are

$$2.10 \times 10^{-2} \text{ mmol} - 3.00 \times 10^{-3} \text{ mmol} = 1.80 \times 10^{-2} \text{ mmol}$$

Convert these values to molarities by dividing by the total solution volume:

$$[A] = [B] = 0.0180 \text{ mmol} / 20.0 \text{ mL} = 9.00 \times 10^{-4} \text{ M}$$

Thus, $K_c = [C] / [A][B] = (1.50 \times 10^{-4}) / (9.00 \times 10^{-4})^2 = 185$

PRE-LAB EXERCISES (It will be helpful to read the entire experiment first.)

1. A 0.010 M solution of a complex ion had an absorbance of 0.25 when measured in a 1.0-cm path-length cuvette. A 0.020 M solution of the same ion had an absorbance of 0.50. What is the molar extinction coefficient of this ion?

2. Ions A and B react to form a complex AB. If 10 mL of 1.0 M A is combined with 10 mL of 1.0 M B, 0.0030 mol of AB is formed. Determine the equilibrium constant for this reaction.

EQUIPMENT: 100-mL volumetric flask, wash bottle, Pasteur pipet and bulb, 11 medium test tubes, burette and stand, burette funnel, 150-mL beaker, test tube rack, spectrophotometer, 6 cuvettes

EXPERIMENTAL

The general procedure for using the spectrophotometer is as follows. The instrument is turned on by rotating the left-hand knob on the front until it clicks; this should be done at least 20 minutes before any measurements are to be made. The wavelength is set using the dial on top of the instrument; in this experiment we will use a wavelength of 450 nm, the wavelength of maximum absorbance of the complex ion. The meter should indicate a reading of 0% transmittance with no sample present and the cover closed. Rotate the left-hand knob on the front of the instrument to adjust the 0% setting. The sample is contained in special test tubes called cuvettes. Fill a clean cuvette half-full with deionized water and wipe the outer surface clean. Insert the cuvette in the sample compartment on top of the instrument such that the index line on the top of the cuvette points toward the front of the instrument (there is a matching mark on the sample compartment). Close the cover. Rotate the right-hand knob until the meter indicates 100% transmittance. For sample measurements, fill a clean cuvette half-full with the sample, wipe the outside, place it in the sample compartment, close the cover, and record the percent transmittance. The %T may be read to more significant figures than the absorbance; the absorbance will be calculated from the %T. If the cuvette is wet from previous use, first rinse it with a small portion of the new solution and discard the rinsings before filling. The 0% and 100% settings should be checked often and readjusted if necessary during the course of the experiment. All measurements should be carried out using the same spectrophotometer.

CAUTION: Two different molarities of iron(III) nitrate solution and two different molarities of potassium thiocyanate are used in this experiment. Be sure that you take the correct solution. Read labels carefully!

Part I. Measure exactly 4.00 mL of 0.00250 M iron(III) nitrate from the stock burette into a 100-mL volumetric flask. Dilute to the mark with deionized water and mix well. Rinse the empty burette at your workstation with about 5 mL of this solution (including the tip), discard the rinsings, and fill the burette. Run a small amount of solution out into a waste beaker in order to fill the tip of the burette; failure to do this will lead to error in your volume measurements.

Label 11 clean, dry test tubes with the numbers 1-11. Use your diluted iron(III) nitrate solution to make up solutions 1-5 according to the information in Table I. The 1.00 M KSCN is contained in a dispenser in the hood. Simply raise the piston all the way and push it down to dispense the required amount of solution. Be careful in measuring out the reagents, as the quality of your results will depend directly upon your accuracy here. Cover each test tube with Parafilm, mix well, and allow to stand for a few minutes before measuring the %T of each solution. Record as many significant figures as possible, being careful to avoid parallax errorsl

Part II. Make up solutions 6-11 using the amounts given in Table II. Be sure that you use the reagents with the correct molarities. Measure the %T of these solutions at 450 nm.

Table I. Solutions for Beer's Law Plot

Soln. No.	Diluted $Fe(NO_3)_3$, mL	1.00 M KSCN, mL	0.1 M HNO_3 , mL
1	1.00	5.00	4.00
2	2.00	5.00	3.00
3	3.00	5.00	2.00
4	4.00	5.00	1.00
5	5.00	5.00	0.00

Table II. Solutions for Equilibrium Constant Determination

Soln. No.	0.00250 M $Fe(NO_3)_3$, mL	0.00250 M KSCN, mL	0.1 M HNO_3 , mL
6	1.00	1.00	5.00
7	1.00	2.00	4.00
8	1.00	3.00	3.00
9	2.00	1.00	4.00
10	2.00	2.00	3.00
11	2.00	3.00	2.00

CALCULATIONS

Part I. Calculate the concentration of $FeSCN^{2+}$ in each of the five solutions. You must take dilution into account, i.e., determine the number of moles of the complex ion (from the initial number of moles of the limiting reagent) and divide by the **total** solution volume to convert to molarity. Convert the percent transmittance of each solution to absorbance. The format of the spreadsheet command for common logarithms is =log(a1) for the logarithm of the value contained in cell A1. Use the Excel spreadsheet to carry out a regression analysis of the molarity-absorbance data and draw a graph of the Beer's Law plot. Use the path length of the cuvette provided by the instructor to calculate the extinction coefficient. Always explain clearly in your report any calculations and formulas which you used in the spreadsheet.

Part II. Use the absorbances of solutions 6-11 along with the slope (and intercept, if nonzero) of the Beer's Law plot to calculate the molarity of $FeSCN^{2+}$ in each solution. The number of moles of the complex ion is then equal to the product of the molarity and the **total** volume of the solution. The numbers of moles of Fe^{3+} and SCN^- remaining must be calculated using the numbers of moles of each species initially present and the number of moles of $FeSCN^{2+}$ formed (moles of reagent remaining = initial moles of reagent minus number of moles reacted). These are also converted to molarity by dividing each by the total volume of the mixture. Calculate the value of K_c for each solution and the average value of the equilibrium constant. Calculate the relative average deviation of the results.

REPORT: Combining the skills you have learned in writing each of the sections of a formal lab report over the past two months, write a formal lab report for today's experiment.