Experiment 16: Spectrophotometric Determination of an Equilibrium Constant

Objective: In this experiment, you will determine the equilibrium constant, K_c, for the formation of the complex $Fe(SCN)^{2+}$. You will also see Le Chatelier's Principle demonstrated.

Introduction

(See Tro, Chapter 14, especially pp 615-629.)

A chemical reaction of the sort expressed by the following chemical equation

$$aA + bB \rightleftharpoons cC + dD$$

actually consists of two competing processes: **the forward reaction**, that is the formation of the products, C and D, from the reactants, and **the reverse reaction**, which is the formation of the reactants, A and B, from the products. When the rates of these two processes equal each other, there is no net change in the concentration of either the products or the reactants, and the reaction is said to be at equilibrium. The ratio of the equilibrium concentrations of the products to the equilibrium concentrations of the reactants is a constant, as shown by the following equation:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Eq. 1

where K_c is the **equilibrium constant**. The brackets signify the concentrations of the various species, and the lower case letters represent the number of moles of each substance involved in the balanced equation. The equilibrium constant is dependent on temperature. Also, reactants and products that appear as pure solids or pure liquids in the chemical equation (as opposed to species in solution) do not appear in the equilibrium constant expression.

You will examine equilibrium conditions of the reaction between iron (III) and thiocyanic acid:

$$Fe^{3+}(aq) + HSCN(aq) \rightleftharpoons FeSCN^{2+}(aq) + H^+(aq)$$

The expression for this equilibrium constant is:

$$K_c = \frac{[FeSCN^{2+}][H^+]}{[Fe^{3+}][HSCN]}$$

Eq. 2

In order to determine the value for this K_c, it is necessary to find the equilibrium concentrations of each of the species involved in the expression. We can carry out the reaction under conditions where the concentration of H^+ remains constant and thus is known. In addition, we can determine the concentration of $FeSCN^{2+}$ spectrophotometrically, and then use this value in calculating the equilibrium concentrations of HSCN and Fe^{3+} knowing their initial concentrations and the stoichiometry of the reaction.

Calculations

The equilibrium concentration of H^+

In all the solutions used in the experiment, $[H^+]$ will be maintained at a value of 0.5 M. Since H^+ will be present in large excess as compared to the other reactants, its concentration will not be appreciably affected by the reaction which occurs and can be assumed to remain constant and equal to 0.5 M.

In addition, the excess of H^+ ions will shift the following equilibrium to the left thus insuring that none of the Fe^{3+} reacts to form other species such as $Fe(OH)^{2+}$:

$$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+$$

Similarly, the thiocyanic acid will remain undissociated as the following equilibrium is also shifted to the left:

$$HSCN \rightleftharpoons SCN^- + H^+$$

The equilibrium concentration for $FeSCN^{2+}$

The value for $[FeSCN^{2+}]$ at equilibrium will be determined from a spectrophotometric measurement employing **Beer's Law** (see Experiment 6):

$$A = \varepsilon c \ell \qquad \textbf{Eq. 3}$$

where A is the absorbance of a solution, ε is the molar absorptivity, c is the concentration of the solution in moles/liter and ℓ is the length of the absorption cell which contains the solution. You and your classmates will prepare a series of standard solutions in order to construct a calibration curve. (A standard solution is one whose concentration is accurately known.) In preparing these standards, an excess of Fe^{3+} ion is used so that all the SCN^- ion is converted to $FeSCN^{2+}$. **Thus after mixing, the concentration of $FeSCN^{2+}$ in the *standard* solution will be equal to the initial concentration of HSCN**. The absorbance of a solution can be measured directly on a spectrophotometer. The wavelength of light must be specified and is usually chosen to coincide with a wavelength wherein the substance absorbs most strongly. In the equilibrium you will examine, the wavelength of choice is 447 nm for the $FeSCN^{2+}$ complex.

Once the absorbance values of these standard solutions have been determined, you will plot absorbance, A, versus concentration, c, for the species $FeSCN^{2+}$. The concentration of $FeSCN^{2+}$ at equilibrium will be determined using this curve and the absorbance values that you obtain for the *equilibrium* solutions.

The equilibrium concentrations for Fe^{3+} and HSCN

It is now necessary to determine the equilibrium concentrations for Fe^{3+} and HSCN. Upon examination of the chemical equation for the reaction, we see that for every mole of $FeSCN^{2+}$ formed, one mole of Fe^{3+} and one mole of HSCN are consumed. Therefore, the equilibrium number of moles of Fe^{3+} or HSCN, is equal to the initial number of moles of Fe^{3+} or HSCN, minus the number of moles of $FeSCN^{2+}$ present at equilibrium.

	Fe^{3+} (aq)	+ HSCN (aq)	$\rightleftharpoons$ $FeSCN^{2+}$ (aq)	+ H^+ (aq)
initial number of moles	a	b	0	
equilibrium number of moles	$a - c$	$b - c$	c	

We can calculate the number of moles of $FeSCN^{2+}$ using the equilibrium concentration obtained from the spectrophotometric measurement. Thus, the concentrations of Fe^{3+} and HSCN at equilibrium can be calculated using the following expressions:

$$[Fe^{3+}] = \frac{a - c}{V}$$

$$[HSCN] = \frac{b - c}{V}$$

Eq. 4

where a = initial number of moles of Fe^{3+}, b = initial number of moles of HSCN, c = number of moles of $FeSCN^{2+}$ at equilibrium and V = total volume of *equilibrium* solution.

The equilibrium constant, K_c

We can now substitute the equilibrium concentrations of all the species into the equilibrium expression (**Eq. 2**) and calculate K_c.

Le Chatelier's Principle (Tro, pp 641-648)

When the conditions of a system at equilibrium are altered, the system responds in such a way as to maintain the equilibrium. In 1888, Henri-Lewis Le Chatelier described this phenomenon in a principle that states, "when a change in temperature, pressure or concentration disturbs a system in chemical equilibrium, the change will be counteracted by an alteration in the equilibrium composition." You will observe this principle at work in the reversible reaction between the iron (III) ion and the thiocyanate ion:

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

You will selectively alter the concentration of one of the ions by adding a reagent that reacts to form an insoluble salt with the ion, causing it to precipitate out of solution. In addition, you will observe the effect that a temperature change has on the solution at equilibrium, which will allow you to conclude whether the reaction is exothermic or endothermic.

Procedure for the Determination of the Equilibrium Constant

Wear safety glasses at all times.

Read about pipets in TECH II.D. **NEVER** pipet a solution directly out of the bottle, or it is likely to become contaminated. Pour some of the solution into a beaker before pipeting.

Notice! There are two different concentrations of $Fe(NO_3)_3$ used in this experiment. Read the label of the bottle that you are using carefully to be sure it is the right one!

Preparing the standard solutions

You and one or two other students will be assigned to use a particular spec. You must measure the absorbances of all the standard solutions on the same spec, and later you must also use this spec to measure the absorbances of your own equilibrium mixtures. Your instructor will assign your group to prepare a standard solution from the table shown below. Dispense the amount of HSCN shown in the table from the dispensing buret into a 100 mL volumetric flask and dilute to the mark with 0.200 M $Fe(NO_3)_3$ in 0.500 M HNO_3 solution (**not** 0.002 M!) (see TECH Section II.G).

Never put acetone into a cuvet as it will "cloud" the plastic. Review how to use the spectrophotometer in TECH Section V. You must use the same spec for *all* absorbance readings. Set the wavelength of the spec to **447 nm**.

"Zero" the spec using the 0.200 M $Fe(NO_3)_3$ in 0.500 M HNO_3 solution as a blank, and determine the absorbance of your assigned standard solution. Use the standard solutions prepared by other groups to obtain absorbance measurements for all of the standard solutions using your group's spec.

Solution	number of mL of 0.00200 M HSCN in 0.500 M HNO_3
A	1.00
B	2.00
C	3.00
D	4.00
E	5.00
F	6.00

Preparing the equilibrium solutions

Each student must prepare his/her own equilibrium solutions following the procedure below.

Label three *clean, dry* 18 x 150 mm test tubes as "2", "3" and "5". Obtain about 35 mL of 0.00200 M $Fe(NO_3)_3$ in 0.500 M HNO_3 solution (**not** 0.200 M!) in a *clean, dry* 250 mL beaker. Label the beaker. Rinse a 5.00 mL *volumetric* pipet with small portions of this solution. Use this pipet to add 5.00 mL of this solution to each test tube.

Into each of the labeled test tubes and using the dispensing buret, you will dispense 0.00200 M HSCN in 0.500 M HNO_3 solution. Deliver the exact number of milliliters (2, 3 or 5) indicated on the label of the test tube and record the volume delivered.

Obtain about 15 mL of 0.500 M HNO_3 solution in a *clean, dry* 150 mL beaker. Label the beaker. Rinse a *measuring* pipet with this solution, and add enough 0.500 M HNO_3 to each test tube to make the total volume equal to 10.0 mL (3, 2 or 0 mL, depending on the volume of 0.00200 M HSCN in 0.500 M HNO_3 solution which was added). Note that when using a measuring pipet, the liquid is **not** drained to the tip. The flow of liquid is stopped when the desired calibration mark is reached, and the delivered volume is taken as the final reading minus the initial reading. Mix each solution thoroughly with a glass stirring rod. Be sure to dry off the stirring rod after mixing each solution. Immediately proceed with the next step as interfering side reactions may occur as the solutions age.

Use the same spec that you used to measure the standard solutions. "Re-zero" the instrument using the 0.00200 M $Fe(NO_3)_3$ in 0.500 M HNO_3 solution as a blank. Without any delay, measure the absorbance of each equilibrium solution (remember to properly rinse the cuvet!). Note the temperature of the solutions.

Repeat the entire procedure for preparing equilibrium solutions to obtain a second set of data. (Re-zero the instrument with the 0.00200 M $Fe(NO_3)_3$ in 0.500 M HNO_3 solution, in case the instrument has drifted.) In the end, you should have a total of six absorbance readings for equilibrium solutions.

Rinse out the cuvet and dispose of it in the trash when you are finished.

Procedure for the Demonstration of Le Chatelier's Principle

Prepare a water bath by heating a beaker of water to 70-80°C on a hot plate.

Place 1 drop of 1 M $Fe(NO_3)_3$ solution in a clean 18 x 150 mm test tube, and add 1 drop of 1 M KSCN. Add 12 mL of water and thoroughly mix the contents of the test tube. Record your observations. Divide the mixture into 2 mL portions in six 18 x 150 mm test tubes. One of the test tubes will remain untouched and serves as a "control" against which the other test tubes can be compared.

1. To the first test tube, add 3 drops of 0.1 M $AgNO_3$ solution. Shake to mix. Record your observations. Next add 3 drops of 1 M $Fe(NO_3)_3$, shake to mix and record your observations. Place the contents of this test tube in the **Laboratory Byproducts** jar labeled **Silver**.
2. To the second test tube, add 3 drops of 0.1 M $AgNO_3$ solution. Shake to mix. Record your observations. Next add 3 drops of 1 M KSCN, shake to mix and record your observations. Place the contents of this test tube in the **Laboratory Byproducts** jar labeled **Silver**.
3. To the third test tube, add 3 drops of 0.5 M K_2HPO_4 solution. Shake to mix. Record your observations. Next add 3 drops of 1 M $Fe(NO_3)_3$, shake to mix and record your observations. The contents of this test tube may be poured down the drain.
4. To the fourth test tube, add 3 drops of 0.5 M K_2HPO_4 solution. Shake to mix. Record your observations. Next add 3 drops of 1 M KSCN, shake to mix and record your observations. The contents of this test tube may be poured down the drain.

5. Place the fifth test tube in the 70-80° water bath for 1-2 minutes. Compare the warm solution to the solution in the unheated test tube (the "control"), and record your observations. The contents of this test tube, as well as the control, may be poured down the drain.

Clean off your lab bench before you leave.

Calculations

1. a) Calculate the $FeSCN^{2+}$ concentrations of the standard solutions using an appropriate dilution factor. [Note: Remember that all of the HSCN is converted to $FeSCN^{2+}$ in the standard solutions.]

   b) Plot the absorbance, A, versus the $FeSCN^{2+}$ concentration of the *standard* solutions. From this calibration curve, determine the concentration of $FeSCN^{2+}$ in each of the *equilibrium* solutions you prepared using their absorbance values. You should use the computer, the program Excel and the LINEST function to plot and analyze this data. You should report **6** values for $[FeSCN^{2+}]_{eq}$.

   c) Calculate the number of moles of $FeSCN^{2+}$ (*c* in **Eq. 4**) present at equilibrium in each equilibrium mixture from the concentrations determined in b) above. Report **6** values.

2. Calculate the initial number of moles of Fe^{3+} (*a* in **Eq. 4**) and HSCN (*b* in **Eq. 4**) placed in each equilibrium solution before reaction.

3. Calculate the equilibrium concentrations of Fe^{3+} and HSCN using **Eq. 4**. Report **6** values for each.

4. Determine the value of K_c for each of your mixtures. Report **6** values.

Questions

1. Of the values that you calculated for K_c, do you consider one of them to be the "best" value? Explain why or why not. Does your data indicate that K_c is independent of the initial concentrations of the reactants?

2. List important sources of error in the determination of K_c and the effect that each would have on your results.

Note: For questions 3-5, be sure you know the color of the reactants, Fe^{3+} and SCN^-, and the product, $FeSCN^{2+}$.

3. a) Did the addition of $AgNO_3$ cause an increase in the concentration of the product or the reactants? Explain what observation leads you to this conclusion.

   b) Following the addition of $AgNO_3$, which ion then caused an increase in the concentration of the product: Fe^{3+} or SCN^-? Again, give evidence for your answer.

   c) With what did $AgNO_3$ react, and what compound was formed? Discuss all the evidence that supports the formation of this compound.

4. a) Did the addition of K_2HPO_4 cause an increase in the concentration of the product or the reactants? Explain what observation leads you to this conclusion.

b) Following the addition of K_2HPO_4, which ion then caused an increase in the concentration of the product: Fe^{3+} or SCN^-? Again, give evidence for your answer.

c) With what did K_2HPO_4 react, and what compound was formed? Discuss all the evidence that supports the formation of this compound.

5. Based on your observations of the solution in the test tube that was heated, do you think the forward reaction is endothermic or exothermic? Explain.
(**Hint:** see Tro, pp 646-647.)