

## 14A. Le Châtelier's Principle

### Introduction

All chemical reactions proceed until equilibrium is reached, provided none of the reactants or the products are removed from the reaction mixture. Le Châtelier's principle describes what happens to an equilibrium after it has been disturbed (Ebbing/Gammon, Sections 14.7, 14.8, and 14.9).

### Purpose

You will study the application of Le Châtelier's principle by seeing the effect of the addition of  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  to an equilibrium mixture of  $\text{Fe}^{3+}$ ,  $\text{SCN}^-$ , and  $\text{Fe}(\text{SCN})^{2+}$ ; the effect of the addition of an acid to an equilibrium mixture of  $\text{Ni}^{2+}$ ,  $\text{NH}_3$ , and  $\text{Ni}(\text{NH}_3)_6^{2+}$ ; the effect of the addition of an acid and a base on the equilibrium involving an indicator; the effect of acids and bases on the solubility of  $\text{Ca}(\text{OH})_2$  in water; and the effect of temperature on an equilibrium mixture of  $\text{Co}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{CoCl}_4^{2-}$ .

### New Substances

In this experiment you will encounter some substances that you may not have seen before. The reaction between  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  (thiocyanate ion) gives  $\text{Fe}(\text{SCN})^{2+}$ . This substance is a deeply colored complex ion. Other complex ions that you will encounter are  $\text{Ni}(\text{NH}_3)_6^{2+}$  and  $\text{CoCl}_4^{2-}$ . These substances result from the reaction between  $\text{Ni}^{2+}$  and  $\text{NH}_3$  and from the reaction between  $\text{Co}^{2+}$  and  $\text{Cl}^-$ , respectively. You will also study an equilibrium involving methyl orange, an indicator. Indicators are discussed in Appendix D. Read the second, third, and fourth paragraphs of that appendix to gain an understanding of this indicator.

### Concept of the Experiment

Le Châtelier's principle can be described in the following way: "When a system in chemical equilibrium is disturbed by a change of temperature, pressure, or concentration, the system shifts in equilibrium composition in a way that tends to counteract this change of variable" (Ebbing/Gammon, Section 14.7). This statement explains the effects that you will encounter in this experiment.

### Procedure

#### Getting Started

1. Obtain 3 small test tubes and a piece of filter paper.
2. Obtain directions for discarding the solutions that you will use in this experiment.
3. Take care in handling the solutions used in this experiment.

**CAUTION:** Solutions of ammonia, hydrochloric acid, and sodium hydroxide can cause chemical burns, in addition to ruining your clothing. Do not use your finger as a stopper when mixing these solutions. If you spill any of these solutions on you, wash the contaminated area thoroughly and report the incident to your laboratory instructor. You may require further treatment.

### **Studying the Equilibrium of $\text{Fe}^{3+}$ and $\text{SCN}^-$ with $\text{Fe}(\text{SCN})_2^{2+}$**

1. Mark each of the test tubes with an identification number (1, 2, and 3).
2. Add 20 mL of distilled water from a graduated cylinder to a 100-mL beaker. Next add 20 drops of 0.1 M  $\text{Fe}(\text{NO}_3)_3$  and 20 drops of 0.1 M  $\text{KSCN}$  to the beaker. The color is due to the  $\text{Fe}(\text{SCN})_2^{2+}$  ion. Stir the solution thoroughly.
3. Using a 10-mL graduated cylinder, add 3 mL of this solution to each of the test tubes.
4. Add 20 drops of 0.1 M  $\text{Fe}(\text{NO}_3)_3$  to test tube 1. Mix by gentle shaking.
5. Add 20 drops of 0.1 M  $\text{KSCN}$  to test tube 2. Mix by gentle shaking.
6. Add 20 drops of distilled water to test tube 3 and mix. The color of the contents of this tube will serve as your reference.
7. Compare the colors in test tubes 1 and 2 with the color in the reference test tube. The intensity of the color in each test tube will indicate the relative concentration of  $\text{Fe}(\text{SCN})_2^{2+}$  in that test tube. For best results, view the test tubes down their lengths against a white paper. Record your observations.

### **Studying the Equilibrium of $\text{Ni}^{2+}$ and $\text{NH}_3$ with $\text{Ni}(\text{NH}_3)_6^{2+}$**

1. Add 10 drops of 0.1 M  $\text{Ni}(\text{NO}_3)_2$  to a clean test tube. Record the color.
2. Add drops of 6 M  $\text{NH}_3$  until the color changes and intensifies. Record the color.
3. Add drops of 6 M  $\text{HCl}$  until the color changes once again. Record the color. The acid has reacted with  $\text{NH}_3$  to form  $\text{NH}_4^+$  ions.

### **Studying the Equilibrium Involving Methyl Orange**

1. Mark each of two small beakers with an identification letter (A for acid and B for base).
2. Add 10 mL of distilled water and 4 drops of 6 M  $\text{HCl}$  to the beaker marked A. Swirl.
3. Add 10 mL of distilled water and 4 drops of 6 M  $\text{NaOH}$  to the beaker marked B. Swirl.
4. Add 1 mL of distilled water to a clean test tube. Then add 4 drops of the indicator solution and 2 drops of the dilute acid solution. Shake gently. Record the color.
5. Add drops of the dilute base solution until the color changes. Shake gently. Record the color.
6. Add drops of the dilute acid solution until the color changes again. Shake gently. Record the color.

**Studying the Solubility of  $\text{Ca}(\text{OH})_2$** 

1. Using a 10-mL graduated cylinder, add 5 mL of 6 M NaOH to a small, clean beaker.
2. Rinse the graduated cylinder, and then use it to add 5 mL of 1 M  $\text{Ca}(\text{NO}_3)_2$  to the same beaker.
3. Stir the mixture thoroughly with a stirring rod. A white precipitate of  $\text{Ca}(\text{OH})_2$  should be present.
4. Using gravity filtration (described in the Introduction to this manual), filter the mixture. This filtration may require a rather long time. While you are waiting, you may wish to begin your study of the equilibrium involving  $\text{CoCl}_4^{2-}$ .
5. Wash the precipitate on the filter paper with 5 mL of distilled water.
6. With a metal spatula, remove as much of the wet precipitate from the filter paper as you can. Suspend this solid in 10 mL of distilled water in a small, clean beaker.
7. Add 2 mL of 6 M HCl and stir the contents of the beaker thoroughly. Record the results.
8. Add 5 mL of 6 M NaOH to the beaker. Record the results. You should be able to deduce the identity of the substance that is formed.

**Studying the Equilibrium of  $\text{Co}^{2+}$  and  $\text{Cl}^-$  with  $\text{CoCl}_4^{2-}$** 

1. Set up a ring stand with an iron ring. Place a piece of wire gauze on the ring. Adjust the height of the ring so that the wire gauze will be in the hottest part of the flame from a laboratory burner. Do not light the burner until this adjustment has been made.

**CAUTION: Avoid burning your fingers. Do not touch the iron ring or the wire gauze at any time while the flame is being used.**

2. Place a small beaker containing distilled water on the wire gauze, and heat the water to a *gentle* boil.
3. Add 5 drops of 0.1 M  $\text{Co}(\text{NO}_3)_2$  to a clean test tube. Record the color.
4. Add 5 drops of concentrated HCl (do not use 6 M HCl). Shake the test tube gently, and record the color. This is the characteristic color of the  $\text{CoCl}_4^{2-}$  ion.
5. Add 5 drops of distilled water. Shake gently. Record the color.
6. Place the test tube in the boiling water, and wait a few minutes until the color has changed again. Record the color.
7. Cool the test tube in cold water or ice until the color changes once more. Record the color.

**CAUTION: Make sure that your gas outlet and those of your neighbors are closed before you leave the laboratory.**

Date: \_\_\_\_\_  
Course/Section: \_\_\_\_\_  
Instructor: \_\_\_\_\_

Student name: \_\_\_\_\_  
Team members: \_\_\_\_\_

## Le Châtelier's Principle

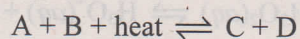
### Prelaboratory Assignment

1. Define the following terms:

a. Chemical equilibrium

b. Le Châtelier's principle

2. Consider the hypothetical reaction



What will happen to the concentrations of A, B, C, and D under each of the following conditions?

a. A catalyst is added to the system, which is at equilibrium.

b. Either C or D is added to the system, which is initially at equilibrium.

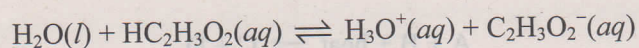
c. Either C or D is removed from the system, which is initially at equilibrium.

d. Either A or B is added to the system, which is initially at equilibrium.

e. The system, which is initially at equilibrium, is cooled.

f. The system, which is initially at equilibrium, is heated.

3. Consider the equilibrium



Why will the addition of NaOH to a solution of acetic acid cause the concentration of the acetate ion ( $\text{C}_2\text{H}_3\text{O}_2^-$ ) to increase?

4. Write chemical equations that describe the equilibria that you will observe during this experiment.

Results

1. The equilibrium of  $Fe^{3+}$  and  $SCN^-$  with  $Fe(SCN)^{2+}$

Compare the colors in the following pairs of test tubes.

1 and 3 \_\_\_\_\_

5. What special safety precautions are cited in this experiment?

2. The equilibrium of  $Ni^{2+}$  and  $NH_3$  with  $Ni(NH_3)_6^{2+}$

Color before addition of  $NH_3$ : \_\_\_\_\_

Color after addition of  $NH_3$ : \_\_\_\_\_

Color after addition of  $HCl$ : \_\_\_\_\_

3. The equilibria involving methyl orange

Color before addition of dilute  $HCl$ : \_\_\_\_\_

Color after addition of dilute  $NaOH$ : \_\_\_\_\_

Color after addition of dilute  $HCl$ : \_\_\_\_\_

4. The solubility of  $Ca(OH)_2$

Give the result obtained when  $HCl$  is added to a suspension of  $Ca(OH)_2$  in water.

Give the result obtained when  $NaOH$  is added and the identity of the substance that is formed.

Date: \_\_\_\_\_  
Course/Section: \_\_\_\_\_  
Instructor: \_\_\_\_\_

Student name: \_\_\_\_\_  
Team members: \_\_\_\_\_

## Le Châtelier's Principle

### Results

1. *The equilibrium of  $Fe^{3+}$  and  $SCN^-$  with  $Fe(SCN)^{2+}$*   
Compare the colors in the following pairs of test tubes.

1 and 3: \_\_\_\_\_

2 and 3: \_\_\_\_\_

2. *The equilibrium of  $Ni^{2+}$  and  $NH_3$  with  $Ni(NH_3)_6^{2+}$*

Color before addition of  $NH_3$ : \_\_\_\_\_

Color after addition of  $NH_3$ : \_\_\_\_\_

Color after addition of HCl: \_\_\_\_\_

3. *The equilibrium involving methyl orange*

Color before addition of dilute HCl: \_\_\_\_\_

Color after addition of dilute NaOH: \_\_\_\_\_

Color after addition of dilute HCl: \_\_\_\_\_

4. *The solubility of  $Ca(OH)_2$*

Give the result obtained when HCl is added to a suspension of  $Ca(OH)_2$  in water.

Give the result obtained when NaOH is added and the identity of the substance that is formed.

5. The equilibrium of  $\text{Co}^{2+}$  and  $\text{Cl}^-$  with  $\text{CoCl}_4^{2-}$

Initial color: \_\_\_\_\_

Color after addition of HCl: \_\_\_\_\_

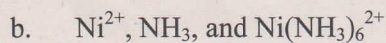
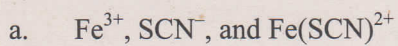
Color after addition of  $\text{H}_2\text{O}$ : \_\_\_\_\_

Color after heating: \_\_\_\_\_

Color after cooling: \_\_\_\_\_

### Questions

1. Use Le Châtelier's principle to explain the different colors found in the following equilibria. Show all chemical reactions.





Student name: \_\_\_\_\_ Course/Section: \_\_\_\_\_ Date: \_\_\_\_\_

c. Methyl orange

## Introduction

Equilibrium in gaseous reactions, homogeneous equilibria for substances in solution, and heterogeneous equilibria between solids and substances in solution occur frequently. All types of homogeneous and heterogeneous equilibria are important in the laboratory and in industrial, geological, agricultural, and biological chemistry. Examples of some of these equilibria appear in your textbook. You will find that the principles of equilibria (Leibing/Gamson, Chapter 14) are applicable to all homogeneous and heterogeneous equilibria.

## Purpose

This experiment will give you an opportunity to determine the equilibrium constant for the formation of  $\text{Fe}(\text{SCN})^{2+}$ . Moreover, the experiment will require you to use Le Châtelier's principle.

**Concepts to be tested:** Equilibrium constant, Le Châtelier's principle, endothermic reaction, color change.

2. a. How does Le Châtelier's principle explain the result you obtained when you added HCl to a suspension of  $\text{Ca}(\text{OH})_2$  in water?

The product is a complex ion that has a coordinate covalent bond between the iron atom and an atom (probably the S atom) from the thiocyanate anion. The color of this complex ion is so intense that micrograms of iron can be detected very easily. Inversely,  $\text{Fe}(\text{SCN})^{2+}$  appears to acid solids in solution. Solid compounds containing this ion have never been isolated.

The objective of this experiment is to determine the equilibrium constant for this reaction. The equilibrium constant is given by the expression

$$K = \frac{[\text{Fe}(\text{SCN})^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^{-}]}$$

where the concentrations of the substances are those at equilibrium. If these concentrations are

- b. How does Le Châtelier's principle explain the result you obtained after the addition of NaOH?

Because  $\text{Fe}(\text{SCN})^{2+}$  is a weakly colored complex ion, it is difficult to measure its concentration directly. You will use a spectrophotometer (Appendix C) to measure the absorbance due to the complex ion without interference from the reactants. The absorbance ( $A$ ) is proportional to the concentration ( $c$ ) of the species that absorbs the light—in this case,  $\text{Fe}(\text{SCN})^{2+}$ —according to Beer's law,  $A = \epsilon c l$ . Beer's law and the usual method for the determination of  $K$  (not to be confused with the equilibrium constant  $K$ ) are discussed in Appendix C. If you did the experiment "The Absorption Spectrum of Cobalt(II) Chloride," you already know a great deal about using this law. After the concentration of  $\text{Fe}(\text{SCN})^{2+}$  has been measured by way of the absorbance, the concentrations of the reactants can be inferred from their starting concentrations and the concentration of the complex ion.

There is a problem, however. To determine  $K$ , we must measure the absorbances of a series of solutions with known amounts of the complex ion. How can known amounts of  $\text{Fe}(\text{SCN})^{2+}$  be obtained? After all, this substance is an active participant in the equilibrium with  $\text{Fe}^{3+}$  and  $\text{SCN}^{-}$  ions. Stoichiometric analysis of the quantities of the reactants will not yield a known amount of the product.

3. a. Why did adding water to the equilibrium involving  $\text{CoCl}_4^{2-}$  cause the color to change? Think carefully.

Initial color: \_\_\_\_\_

Color after addition of HCl: \_\_\_\_\_

Color after addition of  $\text{H}_2\text{O}$ : \_\_\_\_\_

Color after heating: \_\_\_\_\_

Color after cooling: \_\_\_\_\_

### Questions

1. Use Le Châtelier's principle to explain the different colors found in the following equilibria. Show all chemical reactions.
- b. The formation of  $\text{CoCl}_4^{2-}$  from  $\text{Co}^{2+}$  and  $\text{Cl}^-$  is endothermic. Are the color changes that accompany heating and cooling of the equilibrium mixture in accord with Le Châtelier's principle? Explain.

## 14B. Determining an Equilibrium Constant

### Introduction

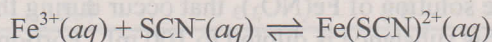
Equilibria in gaseous reactions, homogeneous equilibria for substances in solution, and heterogeneous equilibria between solids and substances in solution occur frequently. All forms of homogeneous and heterogeneous equilibria are important in the laboratory and in industrial, geological, agricultural, and biological chemistries. Examples of some of these equilibria appear in your textbook. You will find that the principles of equilibria (Ebbing/Gammon, Chapter 14) are applicable to all homogeneous and heterogeneous equilibria.

### Purpose

This experiment will give you an opportunity to determine the equilibrium constant for the formation of  $\text{Fe}(\text{SCN})^{2+}$ . Moreover, the experiment will require you to use Le Châtelier's principle.

### Concept of the Experiment

When the reaction between  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  (thiocyanate) ions in aqueous solution comes to equilibrium, the system consists of the reactants and  $\text{Fe}(\text{SCN})^{2+}$ . The chemical equation for this reaction is



The product is a complex ion that has a coordinate covalent bond between the iron atom and an atom (probably the S atom) from the thiocyanate anion. The color of this complex ion is so intense that thiocyanate ions can be used to detect very small quantities of  $\text{Fe}^{3+}$ . Interestingly,  $\text{Fe}(\text{SCN})^{2+}$  appears to exist solely in solution. Solid compounds containing this ion have never been isolated.

The objective of this experiment is to determine the equilibrium constant for this reaction. The equilibrium constant is given by the expression

$$K = \frac{[\text{Fe}(\text{SCN})^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]}$$

where the concentrations of the substances are those at equilibrium. If these concentrations are measured or inferred,  $K$  can be calculated easily.

Because the reactants are essentially colorless, whereas the complex ion is deeply colored, you will use a spectrophotometer (Appendix C) to monitor the absorbance due to the complex ion without interference from the reactants. The absorbance ( $A$ ) is proportional to the concentration ( $c$ ) of the species that absorbs the light—in this case,  $\text{Fe}(\text{SCN})^{2+}$ —according to Beer's law,  $A = kc$ . Beer's law and the usual method for the determination of  $k$  (not to be confused with the equilibrium constant  $K$ ) are discussed in Appendix C. If you did the experiment "The Absorption Spectrum of Cobalt(II) Chloride," you already know a great deal about using this law. After the concentration of  $\text{Fe}(\text{SCN})^{2+}$  has been measured by way of the absorbance, the concentrations of the reactants can be inferred from their starting concentrations and the concentration of the complex ion.

There is a problem, however. To determine  $k$ , we must measure the absorbances of a series of solutions with known amounts of the complex ion. How can known amounts of  $\text{Fe}(\text{SCN})^{2+}$  be obtained? After all, this substance is an active participant in the equilibrium with  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  ions. Stoichiometric analysis of the quantities of the reactants will not yield a known amount of the product.

This difficulty can be avoided. Le Châtelier's principle (Ebbing/Gammon, Section 14.7) indicates that a net reaction from left to right (that is, in the forward direction) can be achieved when more of a reactant is added. As more and more of the same reactant is added, more and more of the product forms. It is possible to add so much of this reactant that essentially all of the other reactant is converted to the product. You will use limiting quantities of  $\text{SCN}^-$  and overwhelming amounts of  $\text{Fe}^{3+}$  to achieve this result. The amount of  $\text{Fe}(\text{SCN})^{2+}$  that is formed will then be essentially identical to the starting amount of the limiting reactant.

In this manner, you will prepare a series of solutions with known concentrations of  $\text{Fe}(\text{SCN})^{2+}$ . You will measure the absorbances of these solutions at 450 nm, the wavelength of maximum absorbance. When these absorbances are plotted against the concentrations of  $\text{Fe}(\text{SCN})^{2+}$  on a graph,  $k$  can be determined from the slope of the straight line (see Appendix C) using linear regression. You may do this calculation by hand, or, if your laboratory instructor wishes, you may use the tool available online at the student website. Calculation materials can be found at

<http://college.hmco.com/PIC/ebbing9e>

Once  $k$  has been determined, working under these conditions will no longer be advantageous. In fact, you will determine the equilibrium constant  $K$  under conditions in which substantial amounts of both of the reactants and the product are present.

### Doing the Calculation

You will have to account for every dilution in order to do the calculations in this experiment. Consider, for example, the dilutions of the solution of  $\text{Fe}(\text{NO}_3)_3$  that occur during the determination of  $k$ . First, 4.0 mL of a 0.0025 M solution of this substance is diluted to 100 mL. Portions of this solution (1.0 mL to 5.0 mL) are then diluted to 10.0 mL. The concentrations of  $\text{Fe}^{3+}$  that result are the ones to use in determining  $k$ . Do not use the original concentration.

In the determination of  $k$ , you will need to construct a graph in which absorbance appears on the vertical axis and the concentration of  $\text{Fe}(\text{SCN})^{2+}$ , in moles per liter, appears on the horizontal axis. Use Figure C.2 in Appendix C as an exact model.

## Procedure

### Getting Started

1. Your laboratory instructor may ask you to work in a group rather than alone. Be sure to wear approved goggles.
2. Obtain 5 large test tubes and 5 matching rubber stoppers. Wash, rinse, and dry the test tubes and the stoppers.
3. Mark each of the test tubes with an identification number (1 through 5).
4. Obtain directions for discarding the solutions you will use in this experiment.
5. If necessary, obtain instructions for using your spectrophotometer.

**Determining  $k$  in Beer's Law**

1. Use a Mohr pipet to transfer exactly 4.00 mL of 0.0025  $M$  KSCN to 100.0 mL in a volumetric flask. If such a flask is not available, use a 100-mL graduated cylinder. Add distilled water until the bottom of the meniscus coincides with the 100-mL mark on the flask or graduated cylinder. (See Figure I.2 in the Introduction to this manual.) Add the last 0.5 mL from a medicine dropper to make sure that you do not add too much water. Mix the solution thoroughly.
2. Rinse the Mohr pipet several times with this solution. Discard each of these portions.
3. Using this pipet, the KSCN solution you have just prepared, and Table 14B.1, add the specified amount of this solution to each of the numbered test tubes.

Table 14B.1  
Composition of Solutions for Determining  $k$

Test Tube No.	Diluted KSCN (mL)	0.25 $M$ $\text{Fe}(\text{NO}_3)_3$ (mL)	0.1 $M$ $\text{HNO}_3$ (mL)
1	1.0	5.0	4.0
2	2.0	5.0	3.0
3	3.0	5.0	2.0
4	4.0	5.0	1.0
5	5.0	5.0	0

4. Rinse the pipet with 0.25  $M$   $\text{Fe}(\text{NO}_3)_3$  solution. Do not put the pipet directly into the stock bottle.
5. Add the correct amount of the  $\text{Fe}(\text{NO}_3)_3$  solution, as shown in the table, to each test tube.
6. Rinse the pipet with 0.1  $M$   $\text{HNO}_3$  solution. Do not put the pipet directly into the stock bottle.
7. Add the correct amount of the 0.1  $M$   $\text{HNO}_3$  solution, as shown in the table, to each test tube. The volumes of the solutions in the test tubes should now be identical.
8. Insert the rubber stoppers. Mix each test tube thoroughly.
9. Measure and record the absorbance of each solution at 450 nm.

**Determining the Equilibrium Constant**

1. Wash and dry the test tubes and rubber stoppers. Renumber the test tubes (6 through 10).
2. Do not use the diluted solution of  $\text{KMnO}_4$  in this part of the experiment. Use the 0.0025  $M$  solution of this substance instead.
3. Prepare the first five solutions shown in Table 14B.2. Use a properly rinsed Mohr pipet for each addition. After you mix these solutions thoroughly, measure their absorbances at 450 nm, and record your results.

This difficulty can be avoided. Le Châtelier's principle (Ebbing/Gammon, Section 14.7) indicates that a net reaction from left to right (that is, in the forward direction) can be achieved when more of a reactant is added. As more and more of the same reactant is added, more and more of the product forms. It is possible to add so much of this reactant that essentially all of the other reactant is converted to the product. You will use limiting quantities of  $\text{SCN}^-$  and overwhelming amounts of  $\text{Fe}^{3+}$  to achieve this result. The amount of  $\text{Fe}(\text{SCN})^{2+}$  that is formed will then be essentially identical to the starting amount of the limiting reactant.

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In the determination of  $k$ , you will need to construct a graph in which absorbance appears on the vertical axis and the concentration of  $\text{Fe}(\text{SCN})^{2+}$ , in moles per liter, appears on the horizontal axis. Use Figure C.2 in Appendix C as an exact model.

## Procedure

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2. Rinse the Mohr pipet several times with this solution. Discard each of these portions.
3. Using this pipet, the KSCN solution you have just prepared, and Table 14B.1, add the specified amount of this solution to each of the numbered test tubes.

**Table 14B.1**  
Composition of Solutions for Determining  $k$

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2	2.0	5.0	3.0
3	3.0	5.0	2.0
4	4.0	5.0	1.0
5	5.0	5.0	0

4. Rinse the pipet with 0.25  $M$   $\text{Fe}(\text{NO}_3)_3$  solution. Do not put the pipet directly into the stock bottle.
5. Add the correct amount of the  $\text{Fe}(\text{NO}_3)_3$  solution, as shown in the table, to each test tube.
6. Rinse the pipet with 0.1  $M$   $\text{HNO}_3$  solution. Do not put the pipet directly into the stock bottle.
7. Add the correct amount of the 0.1  $M$   $\text{HNO}_3$  solution, as shown in the table, to each test tube. The volumes of the solutions in the test tubes should now be identical.
8. Insert the rubber stoppers. Mix each test tube thoroughly.
9. Measure and record the absorbance of each solution at 450 nm.

**Determining the Equilibrium Constant**

1. Wash and dry the test tubes and rubber stoppers. Renumber the test tubes (6 through 10).
2. Do not use the diluted solution of  $\text{KMnO}_4$  in this part of the experiment. Use the 0.0025  $M$  solution of this substance instead.
3. Prepare the first five solutions shown in Table 14B.2. Use a properly rinsed Mohr pipet for each addition. After you mix these solutions thoroughly, measure their absorbances at 450 nm, and record your results.

Table 14B.2 Composition of Solutions for Determining  $K$ 

Test Tube No.	0.0025 M $\text{Fe}(\text{NO}_3)_3$ (mL)	0.0025 M $\text{KSCN}$ (mL)	0.1 M $\text{HNO}_3$ (mL)
6	1.0	1.0	5.0
7	1.0	1.5	4.5
8	1.0	2.0	4.0
9	1.0	2.5	3.5
10	1.0	3.0	3.0
11	2.0	1.0	4.0
12	2.0	1.5	3.5
13	2.0	2.0	3.0
14	2.0	2.5	2.5
15	2.0	3.0	2.0

- Wash and dry the test tubes. Renumber them (11 through 15), and prepare the remaining solutions. Measure the absorbances of these solutions at the same wavelength, and record your results.

## Procedure

### Getting Started

1. Wash and dry the test tubes and rubber stoppers. Renumber the test tubes (6 through 10) and prepare the first five solutions shown in Table 14B.2. Use a pipet to transfer the solutions to the test tubes. Mix each test tube thoroughly.
2. Measure and record the absorbance of each solution at 450 nm.
3. Prepare the remaining five solutions shown in Table 14B.2. Use a pipet to transfer the solutions to the test tubes. Mix each test tube thoroughly.
4. Measure and record the absorbance of each solution at 450 nm.
5. Record your results.



Date: \_\_\_\_\_  
Course/Section: \_\_\_\_\_  
Instructor: \_\_\_\_\_

Student name: \_\_\_\_\_  
Team members: \_\_\_\_\_

## Determining an Equilibrium Constant

### Prelaboratory Assignment

1. Provide definitions for the following terms:

a. Chemical equilibrium

b. Homogeneous equilibrium

c. Heterogeneous equilibrium

d. Le Châtelier's principle

e. Complex ion

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Instructor: \_\_\_\_\_

f. Beer's law

2. a. What reaction are you studying in this experiment?

b. Give the mathematical expression for the equilibrium constant that pertains to this reaction.

c. What is the difference between  $k$  and  $K$ ?

d. How will Le Châtelier's principle be used to obtain  $k$ ?

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Instructor: \_\_\_\_\_

Student name: \_\_\_\_\_  
Team members: \_\_\_\_\_

## Determining an Equilibrium Constant

### Results

1. *Obtaining data for determining  $k$*

Test Tube No.	$A$
1	_____
2	_____
3	_____
4	_____
5	_____

2. *Obtaining data for determining  $K$*

Test Tube No.	$A$	Test Tube No.	$A$
6	_____	11	_____
7	_____	12	_____
8	_____	13	_____
9	_____	14	_____
10	_____	15	_____

## Questions

1. a. Complete the following table by calculating  $[\text{Fe}(\text{SCN})^{2+}]$  for each test tube and inserting the absorbance as a first step in determining  $k$ . All concentrations are to be given in  $M$ .

Test Tube No.	$[\text{Fe}(\text{SCN})^{2+}]$	$A$
1	_____	_____
2	_____	_____
3	_____	_____
4	_____	_____
5	_____	_____

Representative calculation:

- b. Use the available piece of graph paper to plot these absorbances and values of  $[\text{Fe}(\text{SCN})^{2+}]$ .

Test Tube No.	$A$	Test Tube No.	$A$
11	_____	6	_____
12	_____	7	_____
13	_____	8	_____
14	_____	9	_____
15	_____	10	_____

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- c. Calculate the slope of the best straight line, using linear regression (see Appendix C). Either do the calculation by hand or, if your laboratory instructor wishes, use the tool available online at the student website. If you wish, draw a straight line with this slope on your graph. The line should pass through the origin ( $A = 0$ ,  $[\text{Fe}(\text{SCN})^{2+}] = 0$ ).

No.	[Fe <sup>3+</sup> ]	[SCN <sup>-</sup> ]	[Fe(SCN) <sup>2+</sup> ]	[Fe <sup>3+</sup> ]	[SCN <sup>-</sup> ]	[Fe(SCN) <sup>2+</sup> ]
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
Mean:						

$k =$  \_\_\_\_\_ (Give units.)

2. a. Complete the following table (with all concentrations in  $M$ ).

Test Tube No.	Starting [Fe <sup>3+</sup> ]	Starting [SCN <sup>-</sup> ]	[Fe(SCN) <sup>2+</sup> ]	Equilibrium [Fe <sup>3+</sup> ]	Equilibrium [SCN <sup>-</sup> ]	$K$
6	_____	_____	_____	_____	_____	_____
7	_____	_____	_____	_____	_____	_____
8	_____	_____	_____	_____	_____	_____
9	_____	_____	_____	_____	_____	_____
10	_____	_____	_____	_____	_____	_____
11	Representative calculation:					
12	_____	_____	_____	_____	_____	_____
13	_____	_____	_____	_____	_____	_____
14	_____	_____	_____	_____	_____	_____
15	_____	_____	_____	_____	_____	_____

Mean: \_\_\_\_\_

Representative calculation:

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- b. Determine the precision of your results for  $K$ , using the method shown in Appendix A. Do the calculation by hand, or, if your laboratory instructor wishes, use the tool available online at the student website.
3. Although the use of absorbances at 450 nm provided you with maximum sensitivity, the absorbances at, say, 400 nm or 500 nm are not zero and could have been used throughout this experiment. Would the same value of  $K$  be obtained at one of these wavelengths? Explain.