Determination of an Equilibrium Constant

PURPOSE

To determine the equilibrium constant for the reaction:

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

GOALS

- To gain more practice using a pipet properly.
- To gain more practice diluting stock solutions.
- To gain more practice using a spectrophotometer.
- To gain practice plotting a calibration curve and use it to determine the concentration of an unknown solution.

INTRODUCTION

A typical chemical equation has the following form:

$$aA + bB \rightarrow cC + dD. \tag{1}$$

This form of the equation assumes that the reaction proceeds completely to products. In practice, many reactions do not proceed to completion. If we measure the concentration of a reactant, it eventually reaches a value that does not change further over time. If we measure the concentration of a product, it reaches a constant value short of that predicted by the theoretical yield calculation. In these cases, we say that the reaction has reached **equilibrium**. We write the chemical reaction using equilibrium arrows instead of a single arrow.

$$aA + bB \rightleftharpoons cC + dD \tag{2}$$

At equilibrium, the rates of the forward and reverse reactions are equal and, unless equilibrium is disturbed (stressed), no changes in reactant or product concentrations will be measured. The equilibrium arrows, one of which points in each direction, reinforce this idea.

At equilibrium, the molar concentrations of products and reactants will be fixed in a given ratio. This ratio is the equilibrium constant, K_{eq}, which is determined by substituting molar concentrations (indicated by the square brackets) into the equilibrium constant equation. The general form of this equation is:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}. \quad (3)$$

Reactants mixed in arbitrary concentrations will react until the ratio of the concentrations reaches the value of the equilibrium constant according to equation 3. The value of K_{eq} varies with temperature; therefore, the temperature at which the equilibrium constant was determined must be referenced.

In this laboratory experiment, a combination of solution chemistry, stoichiometry and spectrophotometric analysis will be used to determine the equilibrium constant for a reaction between iron (III) ion (Fe^{3+}) and thiocyanate ion (SCN^-). In acidic solution, these ions form a blood-red complex ion as shown in equation 4.

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq) \quad (4)$$

The equilibrium constant for equation 4 can be expressed using the concentrations of the three components.

$$K = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} \quad (5)$$

In order to calculate the equilibrium constant, one must simultaneously determine the concentrations of all three of the components. In this experiment, you will measure the concentration of $FeSCN^{2+}$ at equilibrium by measuring its absorbance at 470 nm. Since Fe^{3+} and SCN^- do not absorb light at this wavelength, they do not interfere with the measurements. If you know the initial (before equilibrium) concentrations of Fe^{3+} and SCN^-, you can use a reaction table to calculate the equilibrium concentrations of these two ions at equilibrium.

For example, you might initially mix equal volumes of 2.0 *M* Fe^{3+} and 2.0 *M* SCN^-. The term "initial concentration" can be confusing. Even though the reaction appears to go instantaneously upon mixing the reactants, the "initial concentrations" in the reaction table are those after dilution has been taken into consideration but before any reaction occurs. Thus, the initial line in the reaction table for mixing equal volumes of 2.0 *M* Fe^{3+} and 2.0 *M* SCN^- should have entries of 1.0 *M* under Fe^{3+} and SCN^- due to dilution. The initial concentration of $FeSCN^{2+}$ is 0.0 *M*. In our example, you might measure an equilibrium (final) concentration of 0.6 *M* $FeSCN^{2+}$. With the final concentration of the product, you can determine the change in product concentration and, therefore, the changes in the reactant concentrations. The reaction table is shown below.

	Fe^{3+}	+ SCN^-	= $FeSCN^{2+}$
initial	1.0 M	1.0 M	0.0 M
Δ	−0.6 M	−0.6 M	+0.6 M
equilibrium (final)	0.4 M	0.4 M	0.6 M

In this experiment, 0.2 *M* HNO_3 serves as the solvent. The acid adds a large (compared to the reactants) amount of H^+. This prevents side reactions such as the formation of $FeOH^{2+}$, a brownish species that can affect the results. The acid concentration is high enough that it is not

affected by the reaction and remains constant at 0.2 *M*.

You will prepare six standard solutions of $FeSCN^{2+}$ to calibrate a spectrophotometer. A fair question is "How do I know the concentration of $FeSCN^{2+}$ in my standard solutions if it is in equilibrium with Fe^{3+} and SCN^{-}?" In the standard solutions, the concentration of Fe^{3+} is much higher than that of SCN^{-}. This forces the equilibrium as far to the right (toward $FeSCN^{2+}$) as possible. Therefore, the concentration of $FeSCN^{2+}$ in a standard solution will be very nearly equal to the initial concentration of SCN^{-} used in preparing it. The absorbance measurement at 470 nm will correlate to the concentration of complex ion, and an accurate calibration curve (Beer's Law plot) can be obtained. Recall that the calibration curve gives you a relationship between the concentration of a species in solution and its absorbance at a given wavelength: ($A = \epsilon lc$). Using the linear regression of the calibration curve in Part A, you will determine the concentration of $FeSCN^{2+}$ ion in each of five equilibrium mixtures in Part B. An equilibrium constant can then be determined for each mixture; the average should be the equilibrium constant value for the formation of the $FeSCN^{2+}$ ion.

In Part A of this experiment, you will prepare $FeSCN^{2+}$ solutions of known concentrations, measure their absorbances at 470 nm, and produce a calibration curve. In Part B, you will make equilibrium mixtures of Fe^{3+}, SCN^{-}, and $FeSCN^{2+}$. You will determine the concentration of $FeSCN^{2+}$ from its absorbance at 470 nm and your calibration curve from Part A. Then using reaction tables, you will calculate the equilibrium concentrations of Fe^{3+} and SCN^{-}, and determine the equilibrium constant for the formation of $FeSCN^{2+}$.

EQUIPMENT

1 MicroLab spectrophotometer

1 MicroLab spectrophotometer instruction sheet

6 vials

3 serological pipets

1 pipet bulb

3 30 mL beakers for reagents

6 13 × 100 mm test tubes for mixtures

6 stoppers

1 test tube rack

1 250 mL beaker for waste

1 deionized water squirt bottle

REAGENTS

~10 mL 0.100 *M* $Fe(NO_3)_3$ in 0.2 *M* HNO_3

~10 mL 5.00×10^{-4} *M* NaSCN in 0.2 *M* HNO_3

~15 mL 0.002 *M* $Fe(NO_3)_3$ in 0.2 *M* HNO_3

~15 mL 0.002 *M* NaSCN in 0.2 *M* HNO_3

SAFETY

Nitric acid is listed as a corrosive. Corrosives can attack the skin and cause permanent damage to the eyes. Nitric acid and iron(III) nitrate are listed as oxidants. Sodium thiocyanate is listed as toxic and an irritant. With the exception of nitric acid, the concentrations of all these materials are quite low, however. If you spill any of these chemicals on skin or clothing, flush the area immediately with water.

WASTE DISPOSAL

All of the solutions prepared in this experiment, as well as excess NaSCN solution, should be discarded in the waste container. You may wish to have a waste beaker in your work area to collect waste while you are doing the experiment. Make sure it is labeled. Always remember not to overfill the waste bottle. If your waste bottle is full, please alert your lab instructor.

PRIOR TO CLASS

Please read the following section of Lab Safety and Practices:

- Good Lab Practices[1]
- Preparing Graphs[2]

Please read the following section of Lab Equipment:

- Volumetric Glassware[3]

Please review the following videos:

- Safety[4]
- Pipeting Techniques[5]

LAB PROCEDURE

Please print the worksheet for this lab. You will need this sheet to record your data.

Part A: Preparation of Standard Solutions and Beer's Law Plot

1 A spectrophotometer will be set up in your work area. Make sure it is turned on and allow it to warm up.

2 While the spectrophotometer is warming up, obtain three serological pipets, and label a beaker for waste.

[1] ..\practices\manual.html
[2] ..\graphs\manual.html
[3] ..\equipment\manual.html#volumetric glassware
[4] ..\movies\labsafety.html
[5] ..\movies\pipeting.html

3 Obtain about 10 mL of 0.100 *M* $Fe(NO_3)_3$ in 0.2 *M* HNO_3 in a small, clean, dry beaker. Obtain about 10 mL of 5.00×10^{-4} *M* NaSCN in 0.2 *M* HNO_3 in another beaker. Label the solutions so you do not mix them up.

4 Condition one pipet for each of the solutions you obtained in step 3 and one for deionized water. This procedure is shown in the Pipeting Techniques[6] video under Instrumentation and is described in the Volumetric Glassware[7] section of the Introductory Material of this lab manual.

5 Using the conditioned pipets, add the amounts of the Fe^{3+} solution, SCN^- solution and water listed in Table A for the Blank and Solutions 1A - 5A to six labeled test tubes. Stopper each test tube and invert a few times to mix each solution.

6 Once the spectrophotometer is warmed up, take a spectrum with your Blank solution. To condition your vial, carefully pour a small amount of the Blank solution into a vial and pour it out to waste. Refer to the MicroLab spectrophotometer instructions provided in lab.

7 Condition a vial using Solution 1A, refill the vial, measure its absorbance at 470 nm and record this value in Table A. When finished, retain this sample in your vial until you have completed your calibration plot. Students often choose to label a sheet of paper with positions 1A, 2A, etc., placing each vial on the appropriate position.

8 Repeat step 7 for each of the remaining solutions from Table A.

9 The MicroLab software will plot the absorbance of the $FeSCN^{2+}$ solutions as a function of their concentrations. The trendline and R^2 value are displayed. If your plot is linear with an R^2 value of 0.9 or greater, continue the experiment. If your R^2 value is low, consult with your TA. Record the trendline and R^2 value in Table A. Do not close the MicroLab file, as this calibration will be used to determine concentrations in Part B.

10 Safely dispose of the calibration solutions in your labeled waste beaker.

11 Discard any remaining 0.100 *M* $Fe(NO_3)_3$ in 0.2 *M* HNO_3 and 5.00×10^{-4} *M* NaSCN in 0.2 *M* HNO_3 in the labeled waste container. Rinse and dry your beakers for use in Part B.

Part B: Preparation of the Equilibrium Mixtures and Absorbance Measurements

1 Obtain about 15 mL of 0.002 *M* $Fe(NO_3)_3$ in 0.2 *M* HNO_3 in a small, clean, dry beaker. Obtain about 15 mL of 0.002 *M* NaSCN in 0.2 *M* HNO_3 in another beaker. Label the solutions so you do not mix them up.

2 Re-condition your pipets with the new solutions of Fe^{3+} and SCN^-.

3 Using the conditioned pipets, add the amounts of the Fe^{3+} solution, SCN^- solution and water required for Solutions 1B - 5B listed in Table B to five labeled test tubes. Stopper each test tube and invert a few times to mix the solutions.

4 Measure the absorbance of each solution as in Part A and record them in Table B.

[6] ..\movies\pipeting.html
[7] ..\equipment\manual.html#volumetric glassware

5 When you are finished taking measurements, collect all your waste and place it in the waste bottle in the lab, making sure not to overfill it. Rinse and dry all your glassware with water and return it to the set-up area where you found it. Close the MicroLab software.

6 Remember to show your TA your calibration curve, reaction table, and equilibrium constant calculation. Your TA will manually grade the results and enter your score into WebAssign.

7 Before leaving, enter your results in the in-lab assignment. If all results are scored as correct, log out. If not all results are correct, try to find the error or consult with your lab instructor. When all results are correct, note them and log out of WebAssign. The in-lab assignment must be completed by the end of the lab period. If additional time is required, please consult with your lab instructor.