Experiment 8
Determination of an Equilibrium Constant

OUTCOMES

After completing this experiment, the student should be able to:

- use absorbance data to find the concentration of a colored species.
- calculate the concentration of the species in an equilibrium mixture.
- calculate the equilibrium constant for a reaction.

DISCUSSION

A state of chemical equilibrium exists when the rate of the forward reaction is equal to the rate of the reverse reaction. Once equilibrium has been established, the amounts of products and reactants are constant and an equilibrium constant (K_c) can be expressed for the reaction. If the initial concentrations of reactants and products are known, reaction stoichiometry can be used to determine the concentrations of the reactants and products at equilibrium, and thus the equilibrium constant, if just one of the equilibrium concentrations can be measured.

In this experiment, we will study the reaction between iron(III) ion and thiocyanate ion. The reaction that occurs produces a thiocyanoiron(III) complex which gives the mixture a deep red color.

$$\underset{\text{iron(III)}}{Fe^{3+}(aq)} + \underset{\text{thiocyanate}}{SCN^{-}(aq)} \rightleftharpoons \underset{\text{thiocyanoiron(III)}}{FeSCN^{2+}(aq)}$$

The concentrations of the reactants and product at equilibrium depend on the relative amounts of reactants present before the reaction occurs. However, regardless of the initial concentrations, the final equilibrium concentrations must satisfy the following relationship:

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

where the bracketed terms are molar equilibrium concentrations of the different species and K_c is the temperature-dependent equilibrium constant.

Because the thiocyanoiron(III) complex is a deep red color, its concentration in solution can be related to its absorbance using Beer's Law, $A = \varepsilon cl$. The red color of the complex indicates that red wavelengths of light are reflected, so blue and green wavelengths should be absorbed.

Therefore, the blue wavelength of 470 nm will be used in the experiment to monitor the absorbance and concentration of the reaction product.

In order to use Beer's Law, the molar absorptivity, ε, needs to be determined for the thiocyanoiron(III) complex. This can be obtained by measuring the absorbance of a *standard solution* where the concentration of $FeSCN^{2+}$ is known. The standard solution will be obtained by using a mixture that contains an initial 100-fold excess of Fe^{3+} ion in comparison to SCN^-. According to LeChâtlier's Principle, this high concentration of iron(III) ion shifts the reaction far to the right in favor of the product, using up approximately 100% of the thiocyanate ions. Consequently, the $[FeSCN^{2+}]$ in the equilibrium mixture of the standard solution is approximately equal to the original $[SCN^-]$ once the two solutions are mixed together. The $[FeSCN^{2+}]$ for each of the equilibrium mixtures may then be determined from their absorbances and the molar absorptivity calculated for the standard solution.

Once the concentration of the thiocyanoiron(III) complex is known for the equilibrium mixtures, it will be possible to determine the equilibrium concentrations of the reactants. First, the initial concentration of the reactants can be calculated based on the dilution that occurs when the two reactants are mixed together, before any reaction occurs, using initial volume and concentration information. Since the balanced equation above shows that the products and reactants are in a 1:1 mole ratio, any product formed reduces the amount of reactant in the mixture by an equal amount. Thus, the concentration of remaining reactant at equilibrium is determined by

$$[\text{reactant}]_{eq} = [\text{reactant}]_{init} - [\text{product}]_{eq}$$

In this experiment, we will study the chemical equilibrium involved in the formation of $FeSCN^{2+}$ by varying the initial concentrations of Fe^{3+} and SCN^-. After determining the equilibrium concentrations of all species, they will be substituted into the expression for the equilibrium constant to determine whether K_c is really constant from one case to the next.

PROCEDURE

⚠ ***Wear safety glasses or goggles at all times for this experiment.***

⚠ ***Avoid skin contact with the chemicals in this experiment.***

Note: If you are unsure of how to read burets, please ask. You should be able to record all volumes from the burets to two decimal places.

1. Prepare a standard solution which will be used to determine the molar absorptivity of $FeSCN^{2+}$. Use your 10-mL graduated cylinder to measure 9.0 mL 0.200 M $Fe(NO_3)_3$ (from a reagent bottle, read the concentration carefully) into a vial with a screw-top lid. Add 1.0 mL of 0.00200 M KSCN from a buret. Mix well.

2. Obtain six vials with screw-on lids. Prepare the solutions for the equilibrium mixtures as described in Table 1 using 0.00200 *M* $Fe(NO_3)_3$ and 0.00200 *M* KSCN which should be obtained from the burets. Record the exact volumes used from the burets. Be sure to thoroughly mix the contents of each of the six vials before proceeding.

Table 1. Volumes of reagents for each trial.

Vial Number	**1**	**2**	**3**	**4**	**5**	**6**
$Fe(NO_3)_3$ (mL)	1.0	2.0	4.0	5.0	6.0	8.0
KSCN (mL)	9.0	8.0	6.0	5.0	4.0	2.0

3. Connect the colorimeter to the *LabPro* interface. Open the *LoggerPro* application from the desktop or the Start menu. From within *LoggerPro*, open the "Probes & Sensors" fold, then select the "Colorimeter" folder, and finally the "Absorbance-Conc" file.

4. Prepare a blank cuvette by filling it ¾ full with deionized water.

Handling Cuvettes: Examine your cuvette to ensure that the clear sides are free from scratches. Cuvettes should be wiped clean and dry on the outside with a KimWipe before each measurement. Do NOT use a paper towel! Handle the cuvettes near the top of the ribbed sides. Solutions should be free of bubbles. Align the cuvette in the colorimeter so that the light passes through the smooth sides. **To avoid inconsistencies from different cuvettes, only *one cuvette* should be used for the entire experiment.** If you are refilling a cuvette with a different solution, a small amount of the new solution should be used to rinse the cuvette before filling.

5. Place the blank cuvette in the colorimeter and calibrate the colorimeter at a wavelength of 470 nm. While most of the colorimeters used in the chemistry department are the rounded colorimeters which calibrate with the press of a button, you may occasionally encounter an older version which requires manual calibration. If this is the case, ask your instructor how to calibrate the colorimeter.

Calibration of Rounded Colorimeters: Use the arrow buttons to select the desired wavelength. With the blank cuvette correctly positioned in the colorimeter and the lid closed, press the blue "Cal" button on top of the colorimeter. When the red light stops blinking, the colorimeter is calibrated and may be used.

6. Remove and empty the blank cuvette. Rinse the cuvette twice with ~1 mL portions of the standard solution. Fill the cuvette ¾ full. Insert the cuvette with the standard solution into the colorimeter, close the lid and record the absorbance reading. Repeat this step for each of the six equilibrium mixtures from Table 1.

⚠ ***Make sure to remove the cuvette from the colorimeter when done with the experiment.***

⚠ ***Dispose of all chemicals in the proper waste container.***

DATA ANALYSIS

1. Determine the $[SCN^-]$ in the standard solution when mixed with 9.0 mL of 0.200 M Fe^{3+}. Use this concentration to determine the $[FeSCN^{2+}]$ in the standard solution.

2. Calculate the molar absorptivity, ε, of $FeSCN^{2+}$ from the absorbance and concentration of the standard solution.

3. Prepare a spreadsheet in *Excel* that includes six <u>columns</u>, one for each of the six equilibrium mixture vials. The following information should be included as <u>rows</u> for each trial:

    - Volume Fe^{3+} solution used
    - Volume SCN^- solution used
    - Absorbance
    - $[Fe^{3+}]_{init}$ (after dilution, before reaction)
    - $[SCN^-]_{init}$ (after dilution, before reaction)
    - $[FeSCN^{2+}]_{eq}$
    - $[Fe^{3+}]_{eq}$
    - $[SCN^-]_{eq}$
    - K_c calculated
    - Average K_c

4. Calculate the initial molarity for Fe^{3+} and SCN^- in each of the six equilibrium mixture vials. (*Writing formulas in Excel will simplify these calculations--don't be afraid to ask for help.*)

5. Use the molar absorptivity, ε, to determine the $[FeSCN^{2+}]$ in each of the six equilibrium mixture vials. Using the molarity of $FeSCN^{2+}$ at equilibrium in each of the six trials, determine the molarity of each reactant when equilibrium is reached. *Once again, you are encouraged to use formulas in Excel to simplify these calculations.*

6. Use the equilibrium concentrations of the reactants and product to calculate equilibrium constants for each of the six trials. Calculate the average K_c for the six trials.

7. How constant were your K_c values at room temperature? Explain any variation.

8. See if you can find literature and/or internet references for the equilibrium constant for this reaction. Please cite the reference(s). How does our result compare with the one(s) you cited?

POSTLAB ACTIVITY

You will be individually completing a postlab quiz on D2L. While taking the quiz, you will be given data to analyze, so you will need to have access to *Excel* while taking the quiz. Before leaving lab today, your instructor should check your work to make sure that you correctly understand the necessary concepts and calculations before beginning the quiz.