Using Spectrophotometric Methods to Determine an Equilibrium Constant

Introduction

There is a great misconception that all chemical reactions go to completion. This is not so. Usually chemical systems approach what is called an equilibrium state. When a system is at equilibrium, the rate at which products are forming from reactants is exactly the same as the rate at which products are decomposing to produce the reactants. An example of a general reaction can be written as

$$aA + bB \rightleftharpoons cC + dD \tag{1}$$

The equilibrium expression for the reaction above is expressed as

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{2}$$

where K is the equilibrium constant for the reaction at a given temperature. The most important quantity when studying a chemical system at equilibrium is the equilibrium constant. In this experiment, you will study the equilibrium reaction

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

The iron(III) ion reacts with the thiocyanate ion to produce the complex ion thiocyanatoiron(III) which is blood red in color. Other complexes between iron(III) and the thiocyanate ion exist but the complex shown above will predominate since the iron(III) concentration will be high compared to the concentration of the thiocyanate ion. The equilibrium expression is

$$K = \frac{[FeSCN^{2+}]_{eq}}{[Fe^{3+}]_{eq}[SCN^{-}]_{eq}} \tag{4}$$

In order to determine the equilibrium constant for this reaction, the equilibrium concentrations of the three ions in solution must be determined first. The spectrophotometric method is relatively simple and will be the method used in this experiment. In spectrophotometric studies, Beer's Law can be stated as $A = \varepsilon bc$ where **ε** is the molar absorptivity, **b** is the path length in cm, **c** is the concentration in moles/L and **A** is absorbance. At 447 nm, only the thiocyanatoiron(III) complex ion absorbs light and will be the wavelength you will use on your spectrophotometer. This means Beer's Law may now be written as $A = \varepsilon b[FeSCN^{2+}]_{eq}$ which can be rearranged to form

$$[FeSCN^{2+}]_{eq} = \frac{A}{\varepsilon b} \tag{5}$$

Now we must determine $[Fe^{3+}]_{eq}$ and $[SCN^{-}]_{eq}$. It can be assumed that the iron in the system must be present as either Fe^{3+} or $FeSCN^{2+}$. Letting $[Fe^{3+}]_i$ represent the iron **initially** (before reaction) added to the system, then it can be written that $[Fe^{3+}]$ = [Fe3+]$_{eq}$ + $[FeSCN^{2+}]_{eq}$. This equation can be rewritten to give $[Fe^{3+}]_{eq} = [Fe^{3+}]_i - [FeSCN^{2+}]_{eq}$. Substituting the relationship from equation 5 for $[FeSCN^{2+}]_{eq}$, gives the resulting equation

$$[Fe^{3+}]_{eq} = [Fe^{3+}]_i - \frac{A}{\varepsilon b} \qquad (6)$$

Similar statements may be made about the thiocyanate ion. Letting $[SCN^-]_i$ represent the thiocyanate initially added to the system, then it can be written that $[SCN^-]_i = [SCN^-]_{eq} + [FeSCN^{2+}]_{eq}$. This equation can be rewritten to give $[SCN^-]_{eq} = [SCN^-]_i - [FeSCN^{2+}]_{eq}$. Substituting the relationship from equation 5 again for $[FeSCN^{2+}]_{eq}$ gives the resulting equation

$$[SCN^-]_{eq} = [SCN^-]_i - \frac{A}{\varepsilon b} \qquad (7)$$

By substituting equations 5, 6, and 7 into equation 4 the equation obtained is

$$K = \frac{\dfrac{A}{\varepsilon b}}{\left([Fe^{3+}]_i - \dfrac{A}{\varepsilon b}\right)\left([SCN^-]_i - \dfrac{A}{\varepsilon b}\right)} \qquad (8)$$

In this experiment, the pathlength of the cuvette is 1.00 cm and ε of $FeSCN^{2+}$ at 447 nm is taken as 5203 L/mole·cm. By measuring the absorbance of mixtures of various $[Fe^{3+}]_i$ and $[SCN^-]_i$, you will be able to calculate K for each experiment **and** an average K.

NOTE:

You must be very careful not to spill or discard any of your solutions until the experiment is completely finished. All solution transfers **must** be done without losing any solution.

Part I Measuring K

Procedure

1. Pipet 10.00 mL of 2.00×10^{-3} M KSCN solution (record the exact concentration) into a clean 100.0 mL volumetric flask. Pipet 25.00 mL of 2.0 M HNO_3 into the same volumetric flask. Add distilled water to the mark on the flask. Mix the contents thoroughly and transfer all of this solution to a **clean, dry** 250-mL beaker.

2. Obtain **about** 25 mL of 0.100 M $Fe(NO_3)_3$ in a **clean, dry** 50-mL beaker (record the exact concentration). Using a 1.00-mL pipet, add 1.00 mL of the $Fe(NO_3)_3$ solution to the 250-mL beaker containing the KSCN solution. Mix thoroughly by swirling the beaker. Carefully pour some of this solution into the 100-mL volumetric flask used in step 1, swirl, and carefully (without spilling) return the solution to the 250-mL beaker.

3. Set the Spectronic 20 to 447 nm. Set to 100% T (calibrate) with 0.5 M HNO_3 solution as a blank. Using a disposable pipet, fill a cuvette with the solution from step 2 and measure the absorbance.

4. Without spilling, pour the contents of the cuvette back into the beaker. Use the same disposable pipet (above) to remove any drops of solution. Do not rinse.

5. Repeat steps 2 through 4 nine more times (for a total of 10 data points). Draw solution into and out of the disposable pipet a few times after swirling the beaker in step 2. Rinse the cuvette with some of the solution and return it to the beaker. **Do not discard**. Swirl again and continue to step 3. The absorbance should increase each time, **but not linearly**.

6. To test the effect of temperature on the **value** of the equilibrium constant, place the cuvette containing solution 10 in a 50-mL beaker of warm tapwater. Let it stand for 2 minutes and record the temperature. Wipe off the cuvette and record the absorbance of the solution.

Part II Determining Initial Conditions from Known K and Equilibrium Concentrations

Procedure

1. Pipet 10.00 mL of 2.00 x 10^{-3} M KSCN solution into a clean 100.0 mL volumetric flask.

2. Pipet 25.00 mL of 2.0 M HNO_3 into this same volumetric flask. Using a 10.00-mL pipet, add 10.00 mL of the **unknown** $Fe(NO_3)_3$ solution. Add distilled water to the mark on the flask.

3. Measure the absorbance at 447 nm after calibration.

Questions

1. Will the absorbance of the equilibrium mixture (at 447 nm) increase or decrease as Fe^{3+} solution is added? Explain using LeChatelier's principle on equation 3.

2. **In steps 1 and 2 of the procedure**, 10.00 mL of 2.00 x 10^{-3} M SCN^- is diluted to 100.0 mL and placed in a beaker. 0.100 M Fe^{3+} is added to this solution in 10 **1.00 mL increments**. Calculate $[SCN^-]$ and $[Fe^{3+}]$ in the 10 solutions. Consider doing this in a spreadsheet (you will use these values in **Data Treatment and Discussion**), but include one sample calculation in the notebook.

Data Treatment and Discussion

Give a **sample** calculation of $[Fe^{3+}]_i$ (using the **exact** molarity of iron(III)) after addition to the SCN^- solution, $[SCN^-]_i$ (using the **exact** molarity of the SCN^-) after the addition of the iron(III) solution, $[\mathrm{FeSCN}^{2+}]_{\mathrm{eq}}$ from equation 5, where $b = 1.00$ cm and $\varepsilon = 5203$ L/mole·cm, $[\mathrm{Fe}^{3+}]_{\mathrm{eq}}$ from equation 6, $[\mathrm{SCN}^{-}]_{\mathrm{eq}}$ from equation 7 and K, from equation 8, of solution 1.

Using a spreadsheet, set up 7 **clearly labeled** columns with the following.

Column 1	Absorbance, A.
Column 2	$[\mathrm{Fe}^{3+}]_{\mathrm{i}}$
Column 3	$[\mathrm{SCN}^{-}]_{\mathrm{i}}$
Column 4	$[\mathrm{FeSCN}^{2+}]_{\mathrm{eq}}$
Column 5	$[\mathrm{Fe}^{3+}]_{\mathrm{eq}}$
Column 6	$[\mathrm{SCN}^{-}]_{\mathrm{eq}}$
Column 7	$K = \dfrac{[\mathrm{FeSCN}^{2+}]_{\mathrm{eq}}}{[\mathrm{Fe}^{3+}]_{\mathrm{eq}}[\mathrm{SCN}^{-}]_{\mathrm{eq}}}$

Calculate, at the bottom of column 7, the average of the 10 K values. Include the calculation of K for the **warm** solution on the spreadsheet below the average K.

Using the average value of K, the initial concentration of SCN^{-} and the concentration of FeSCN^{2+} (from Beer's law), determine the **original** concentration of Fe^{3+} in the unknown.

Plot $\dfrac{A}{[\mathrm{Fe}^{3+}]_{\mathrm{i}}[\mathrm{SCN}^{-}]_{\mathrm{i}}}$ (as *y*) versus $\dfrac{A([\mathrm{Fe}^{3+}]_{\mathrm{i}} + [\mathrm{SCN}^{-}]_{\mathrm{i}})}{[\mathrm{Fe}^{3+}]_{\mathrm{i}}[\mathrm{SCN}^{-}]_{\mathrm{i}}}$ (as *x*) as an alternate way of determining K that does not rely on knowing the molar absorptivity. A linear trendline (that does **not** go through 0,0) fit to the 10 data points has a slope of **–K**. Compare this K to the average K.

Conclusion

Give the room temperature equilibrium constants (determined by the two methods), the higher temperature equilibrium constant and the concentration of the unknown Fe^{3+} solution. Also address:

> What does the magnitude of the average K suggest (in general terms) about the equilibrium position of the reaction (more toward reactants or toward products).
>
> **Using LeChatelier's Principle**, the average K, and the K of the warm solution, is the reaction of Fe^{3+} with SCN^{-} to form FeSCN^{2+} exothermic or endothermic. Explain.