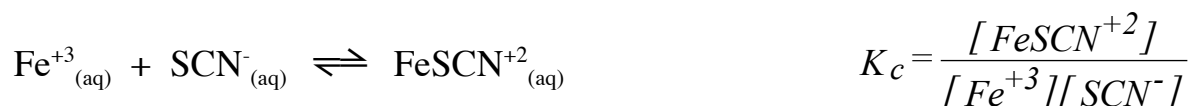


DETERMINATION OF AN EQUILIBRIUM CONSTANT

In this experiment the equilibrium properties of the reaction between the iron(III) ion and the thiocyanate ion will be studied. The relevant chemical equation for this lab is:



When solutions of Fe^{3+} and SCN^{-} are mixed, the above reaction occurs to some extent, forming the *complex ion* FeSCN^{2+} . The concentrations of Fe^{3+} and SCN^{-} will decrease by one mole for every mole of FeSCN^{2+} that forms, but not all of the Fe^{3+} and SCN^{-} ions will be converted to the complex ion under normal circumstances.

The objective of this experiment is to determine the **equilibrium constant, K_c** , for this reaction. The value of K_c is constant at a given temperature. Any mixture of Fe^{3+} and SCN^{-} will react until the same value of K_c is obtained. In this experiment, we will determine K_c for this reaction using several different mixtures of Fe^{3+} and SCN^{-} .

Before we can calculate the value of the equilibrium constant, we must be able to determine the concentration of FeSCN^{2+} in solution. The Beer-Lambert Law, which is commonly referred to as simply **Beer's Law**, relates the absorption of light in a colored sample to its concentration in solution:

$$\mathbf{A} = \boldsymbol{\varepsilon} \mathbf{b} \mathbf{c} = \log (100\% / \%T)$$

Here **A** is the measured absorbance of the colored solution, $\boldsymbol{\varepsilon}$ is the molar absorptivity (with units of $\text{M}^{-1} \text{cm}^{-1}$), **b** is the path length (in cm), and **c** is the concentration (molarity, or moles per Liter) of the species being studied, in this case FeSCN^{2+} . The value of the molar absorptivity, $\boldsymbol{\varepsilon}$, depends on the solute's overall energy stored within the molecule. FeSCN^{2+} has a deep red color while the reactants are virtually colorless, and only FeSCN^{2+} will absorb light in the visible region.

Absorbance is a unitless quantity that corresponds with the amount of light removed by a colored system. We will be using analog Spectronic 21 instruments that determine the **percent transmittance (%T)**, or how much light gets through colored solutions. Calculating absorbance from %T is straightforward ($A = \log (100\%/\%T)$).

Because FeSCN^{2+} has a red color, we will use a wavelength appropriate for measuring red light (**450 nm**). Using the Beer's Law equation, we can determine the molar absorptivity constant, $\boldsymbol{\varepsilon}$, for FeSCN^{2+} by measuring its absorbance at different known concentrations of FeSCN^{2+} . If absorbance is plotted versus concentration, the *slope* will give the molar absorptivity constant using Beer's Law.

Finding the concentration of FeSCN^{2+} can be achieved using Le Chatelier's Principle. If an excess of Fe^{3+} is added to a small amount of SCN^{-} , one can assume that the amount of SCN^{-} present in solution equals the amount of FeSCN^{2+} formed at equilibrium. In other words, we know the final concentration of FeSCN^{2+} in the solution by creating a solution that is not in equilibrium but goes to *completion* using the principle of *limiting reagent*. The SCN^{-} will be completely converted to FeSCN^{2+} , such that the final concentration of FeSCN^{2+} is equal to the initial concentration of SCN^{-} .

The purpose of this lab is to find the value of the equilibrium constant, K_c . First, you will prepare a series of solutions with known concentrations of FeSCN^{2+} (or SCN^{-}) and measure the absorbance values at 450 nm using a Spec 21. When the absorbances are plotted versus the concentration of FeSCN^{2+} , a linear relationship appears, and $\boldsymbol{\varepsilon}$

can be calculated using linear regression (the slope equals ϵb). Remember to report the value of the slope, y-intercept and correlation coefficient when using linear regression. ϵ will allow you to calculate the concentration of FeSCN^{2+} for any combination of Fe^{3+} and SCN^- . You will then prepare a series of solutions with varying amounts of Fe^{3+} and SCN^- initially present, measure the absorbance for FeSCN^{2+} , and determine the value of K_c at room temperature.

PROCEDURE:

Part A: Determining the Molar Absorptivity Constant (ϵ)

Place approximately 30 mL 0.100 M $\text{Fe}(\text{NO}_3)_3$ in 1 M HNO_3 in a dry labeled 100 mL beaker. The HNO_3 allows the solute components to remain in solution, but it does not affect our calculations in this lab. Note also that there are *two different stock solutions* of $\text{Fe}(\text{NO}_3)_3$ and KSCN at different concentrations. Make sure you choose the correct solution for part A or your experiment will not work!

Place approximately 20 mL of 3.00×10^{-4} M KSCN into a second dry labeled 100 mL beaker. Clean and dry six 16 x 150 mm test tubes and label 1-5 and B (blank).

Pipet 5.00 mL of the $\text{Fe}(\text{NO}_3)_3$ solution into tubes 1-5. Pipet 1, 2, 3, 4, or 5 mL of KSCN into the corresponding labeled test tube. Then add the correct number of mL of water to each test tube so that the *total volume* is 10.00 mL. The sixth test tube is the blank and will contain only water.

Determine the %T for each of the five solutions using a Spec 21 at 450 nm. Assume the path length, b , equals 1.00 cm for these trials. Convert the %T readings into absorbance. Recall that $A = \log(100\%/\%T)$.

On your data page, determine the initial molarity of Fe^{3+} and of SCN^- present in each solution using the dilution equation ($M_i \times V_i = M_f \times V_f$).

Example: Find the concentration of SCN^- when 20.0 mL of a 1.50×10^{-4} M KSCN is diluted with 0.1 M HNO_3 to 25.0 mL.

Solution: The initial concentration of KSCN , 1.50×10^{-4} M, is being diluted with nitric acid to a new solution volume of 25.0 mL. We can use $M_i \times V_i = M_f \times V_f$ equation and solve for M_f .
 $M_f = 1.50 \times 10^{-4} \text{ M} \times 20.0 \text{ mL} / 25.0 \text{ mL} = \mathbf{1.20 \times 10^{-4} \text{ M}}$

Find the concentration of FeSCN^{2+} using the law of limiting reactants.

Example: Find the concentration of FeSCN^{2+} when $[\text{SCN}^-] = 1.20 \times 10^{-4}$ M and $[\text{Fe}^{3+}] = 0.100$ M.

Solution: Since $[\text{SCN}^-] \ll [\text{Fe}^{3+}]$, it can be assumed that all of the SCN^- has been converted to FeSCN^{2+} using Le Chatelier's Principle. Hence, the $[\text{FeSCN}^{2+}]$ at equilibrium equals $\mathbf{1.20 \times 10^{-4} \text{ M}}$ in this example. Note that in part B you will be able to use the value of ϵ and the absorbance to calculate $[\text{FeSCN}^{2+}]$.

Construct a graph of absorbance versus the concentration of FeSCN^{2+} . Perform a linear regression on the data, and record your values of the slope, the y-intercept and the correlation coefficient (r). Determine the value of ϵ from the slope. Remember that the path length, b , equals 1.00 cm. **Include this graph** with your final lab report.

Clean your beakers and test tubes between parts A and B. Dispose of the waste in the waste bottle.

Part B: Determining the Equilibrium Constant (K)

Place approximately 30 mL of 2.00×10^{-3} M $\text{Fe}(\text{NO}_3)_3$ in 1 M HNO_3 in a dry labeled 100 mL beaker. Place approximately 20 mL of 2.00×10^{-3} M KSCN in a second dry labeled 100 mL beaker. Clean and dry five 16 x 150 mm test tubes and label 1-5.

Pipet 5.00 mL of the $\text{Fe}(\text{NO}_3)_3$ solution into tubes 1-5. Pipet 1, 2, 3, 4, or 5 mL of KSCN into the corresponding test tube. Then add the correct number of mL of water to each test tube so that the total volume is 10.00 mL.

On your data page, determine the initial molarity of Fe^{+3} and of SCN^- present in each of your five solutions.

Determine the %T for each of the five solutions using the Spec 21 at 450 nm. Assume $b = 1.00$ cm. Convert the %T readings into absorbance values. Dispose of the solutions in the waste bottle when complete.

Calculate the equilibrium concentration of $[\text{FeSCN}^{+2}]_{\text{eq}}$ in each sample. This can be done using Beer's Law and the molar absorptivity constant determined in part A. $c_{\text{FeSCN}} = A / b \epsilon$

Example: Calculate the equilibrium concentration of FeSCN^{+2} when $\epsilon = 3420 \text{ cm}^{-1} \text{ M}^{-1}$, %T = 45.2%, and $b = 1.00$ cm.

Solution: First convert %T to absorbance. $A = \log(100\%/45.2\%) = 0.345$

Now solve for the concentration, c . $c = A / b \epsilon = 0.345 / 1.00 \text{ cm} * 3420 \text{ cm}^{-1} \text{ M}^{-1} = \mathbf{1.00 * 10^{-4} \text{ M}}$

Next, find the equilibrium concentrations of $[\text{Fe}^{+3}]$ and $[\text{SCN}^-]$ using the following equations:

$$[\text{Fe}^{+3}]_{\text{eq}} = [\text{Fe}^{+3}]_{\text{ini}} - [\text{FeSCN}^{+2}]_{\text{eq}} \quad \text{and} \quad [\text{SCN}^-]_{\text{eq}} = [\text{SCN}^-]_{\text{ini}} - [\text{FeSCN}^{+2}]_{\text{eq}}$$

where **eq** = equilibrium concentration and **ini** = initial concentration

Finally, calculate the equilibrium constant, K_c , for each of the five solutions:

$$K_c = [\text{FeSCN}^{+2}]_{\text{eq}} / \{[\text{Fe}^{+3}]_{\text{eq}} * [\text{SCN}^-]_{\text{eq}}\}$$

Determine the average K_c value and deviation in parts per thousand for your calculations.

POSTLAB QUESTIONS:

- A student mixes 5.00 mL of 2.00×10^{-3} M $\text{Fe}(\text{NO}_3)_3$ with 5.00 mL 2.00×10^{-3} M KSCN . She finds that in the equilibrium mixture the concentration of FeSCN^{+2} is 1.40×10^{-4} M.
 - What is the initial concentration in solution of the Fe^{+3} and SCN^- ?
 - What is the equilibrium constant for the reaction?
- Assume that the reaction studied is actually: $\text{Fe}^{+3}_{(\text{aq})} + 2 \text{SCN}^-_{(\text{aq})} \rightleftharpoons \text{Fe}(\text{SCN})_2^+_{(\text{aq})}$
 - What is the equation for determining the equilibrium constant?
 - Using the information from question 1 and assuming $[\text{Fe}(\text{SCN})_2^+] = 1.40 \times 10^{-4}$ M, calculate the equilibrium concentration of Fe^{+3} and SCN^-
 - Determine the numerical value of K .