Spectroscopic Determination of an Equilibrium Constant

Goal and Overview

Iron (III) and thiocyanate ions react to produce iron (III) thiocyanate, a complex ion that appears orange-red in aqueous solution.

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq) \qquad K = \frac{[FeSCN^{2+}]_{eq}}{[Fe^{3+}]_{eq}[SCN^{-}]_{eq}}$$

The spectral profile of aqueous $FeSCN^{2+}$ over the near-UV and short-wave visible wavelength region of the electromagnetic spectrum will be graphed, and the wavelength at which aqueous $FeSCN^{2+}$ absorbs the greatest amount of incident light (λ_{max}) will be extracted from the data and compared to the theoretical value. The proportionality constant between absorption A and $[FeSCN^{2+}]_{eq}$ will be determined using Beer's law and graphical analysis. Equilibrium concentrations of the reactants and product derived from A data will be used to determine an average K at room temperature along with the standard deviation in the individual K values.

Objectives and Science Skills

Perform volumetric dilutions and calculate resulting molarities.
Understand and explain absorption spectroscopy and the mathematical relationships between percent transmittance, absorbance, concentration, path length, and extinction coefficient.
Explain, apply, and analyze linear fitting methods to find relationships between dependent and independent variables, such as absorbance and concentration.
Explain and apply Beer's Law.
Use absorption data to qualitatively and quantitatively analyze the concentration of $FeSCN^{2+}$ in solution.
Identify and discuss factors or effects that may contribute to the uncertainties in values or assessments made from experimental data.

Suggested Review and External Reading

Reference materials and textbook sections covering solutions, dilutions, equilibrium, absorption spectroscopy, and Beer's law

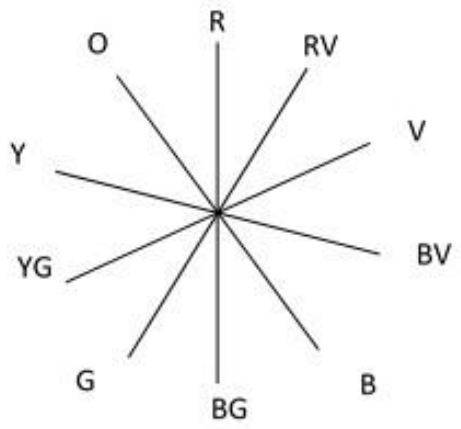
Introduction

This experiment investigates the equilibrium established by the reaction in aqueous solution of iron (III) ions, Fe^{3+}, with thiocyanate ions, SCN^- and the value of the room-temperature equilibrium constant, *K*.

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq) \qquad K = \frac{[FeSCN^{2+}]_{eq}}{[Fe^{3+}]_{eq}[SCN^-]_{eq}}$$

Iron (III) thiocyanate, $FeSCN^{2+}$, appears orange-red in aqueous solution. The depth or intensity of the orange-red color allows for the qualitative assessment of the relative concentrations of $FeSCN^{2+}$ in different solutions. Quantitative analysis of $[FeSCN^{2+}]_{eq}$ is carried out using a Spec 20 UV-visible absorption spectrometer.

The orange-red color of the aqueous $FeSCN^{2+}$ ion indicates that its maximum absorbance lies in the blue/blue-green region of the spectrum. You will use the Spec 20 to scan over a range of wavelengths to identify which wavelength is most strongly absorbed by $FeSCN^{2+}$ (λ_{max}). You will graph absorption versus wavelength to generate a partial spectral profile for aqueous $FeSCN^{2+}$.

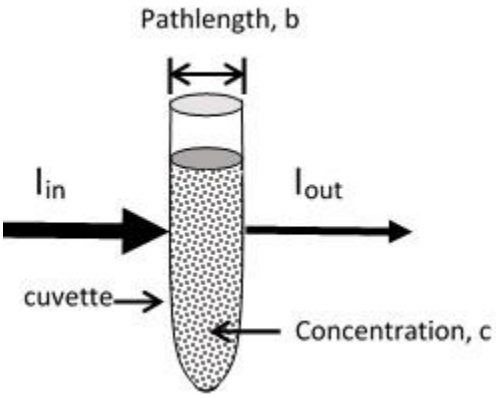


Complementary colors are on opposite sides of the color wheel. When complementary colors are mixed, white light is the result.

When a color is observed (transmitted), its complementary color is absorbed.

R = red, O = orange, Y = yellow, G = green, B = blue, V = violet

In the Spec 20, incident light of a known wavelength at an initial intensity I_{in} is directed through a cuvette containing $FeSCN^{2+}$ solution. The emerging light has a reduced intensity, I_{out}.



The percent transmittance, %T, reflects the ratio of I_{out} to I_{in}, along with the distance the light travels through the sample (pathlength, b, in cm), the number of $FeSCN^{2+}$ ions (concentration, c, in mol/L), and the identity of the absorbing species (molar extinction coefficient, ε, in $\frac{L}{mol \cdot cm}$; ε is molecule- and wavelength-specific).

$$\%T = \left(\frac{I_{out}}{I_{in}}\right)^{-\varepsilon bc} \times 100\%$$

Absorbance, *A*, is defined as the negative $\log_{10}$ of T, and it is the preferred unit because it is directly proportional to concentration.

$$A = -\log_{10}\left(\frac{\%T}{100\%}\right) = \varepsilon bc$$

Graphical analysis can be used to determine the quantitative dependence of *A* on $[FeSCN^{2+}]_{eq}$. As described by Beer's law, a plot of absorbance data for a set of standard solutions with known $[FeSCN^{2+}]_{eq}$ should be linear, with a slope of εb and a y-intercept of (0,0).

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

Without the value of *K,* preparing standard solutions with known $[FeSCN^{2+}]_{eq}$ is not straightforward. Dissolving a salt containing $FeSCN^{2+}$ in water does not work because the ion dissociates as the system comes to equilibrium. There are ways to tailor initial concentrations of Fe^{3+} and SCN^{-} such that the $[FeSCN^{2+}]_{eq}$ can be approximated with some confidence, but there is uncertainty introduced by using such methods that should be discussed when analyzing data and results.

Once the proportionality between A and $[FeSCN^{2+}]_{eq}$ has been determined, whether by finding a value determined in experiments carried out by other researchers and reported in literature or by performing your own experiments, the Beer's law equation can be applied in the opposite direction to calculate $[FeSCN^{2+}]_{eq}$ from A. $[Fe^{3+}]_{eq}$, $[SCN^{-}]_{eq}$, and K can then be calculated.

	$Fe^{3+}(aq)$ +	$SCN^{-}(aq)$ ⇌	$FeSCN^{2+}(aq)$
Initial	$[Fe^{3+}]_{in}$	$[SCN^{-}]_{in}$	0
Change	$-c$	$-c$	$+c$
Equilibrium	$[Fe^{3+}]_{in} - c$	$[SCN^{-}]_{in} - c$	$c = [FeSCN^{2+}]_{eq} = \frac{A}{\varepsilon b}$

$$K = \frac{[FeSCN^{2+}]_{eq}}{[Fe^{3+}]_{eq}[SCN^{-}]_{eq}} = \frac{c}{([Fe^{3+}]_{in} - c)([SCN^{-}]_{in} - c)}, \text{where } c = \frac{A}{\varepsilon b}$$

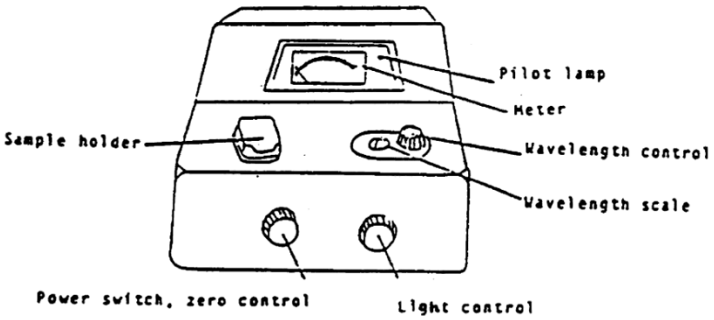
Equipment List

Labeled beakers, test tubes, volumetric flasks
Volumetric pipets, disposable pipets
Spec 20 UV-vis spectrometer, cuvettes (2)
Warm water bath, ice bath
Sodium nitrate solution, 2.0×10^{-3} M $NaNO_3$
Sodium thiocyanate solution, 2.0×10^{-3} M NaSCN
Iron (III) nitrate solution, 2.0×10^{-3} M $Fe(NO_3)_3$

How to Use the Spec 20

You must use the same Spec 20 for the entire experiment.
Cuvettes are NOT test tubes. You only need TWO cuvettes for this experiment.

The power should turned on and the spec should warm up for about 30 minutes before use.



Two cuvettes are needed: one for the blank and one for the sample.
Do not fill cuvettes more than **2/3-3/4 full** (definitely not above the logo).
Hold the cuvette **at the top**. Do not touch the middle (hand oil can interfere with absorption of light).
If the outside of the cuvette is wet or dirty, wipe it gently with **kimwipes**.
Put in cuvette in the holder with the **logo facing forward**.
The sample holder flap must be **closed** when setting 0.0%T and when a cuvette is in it.
Do **not drop or force** the cuvette into the holder; it should slide in easily.
Do not break the cuvette and **do not pour liquid into the Spec 20**.

The measurements are made to one decimal place in % transmittance (%T), not absorption (A). %T is a linear scale so you can estimate between lines; A is on a log scale so you cannot read it accurately.

When making reading, the needle should line up with the mirror section behind where the reading is made so you know you are looking directly down at the needle to make accurate measurements.

The Blank

Make sure the Spec 20 has been on for about 30 minutes.
Set the wavelength with the knob on the top of the Spec 20. Every time the wavelength is changed, you MUST blank.
With the sample holder empty and closed, use the **left knob** (zero control knob) to adjust the needle to **0.0 %T** (left knob, left side).
Put in cuvette containing the blank, close the sample holder flap, and use the **right knob** (light control knob) to adjust the needle to **100.0 %T** (right knob, right side).
Note: at very short wavelengths or very long wavelengths, sometimes you can't get the reading all the way to 100.0%. Usually, that's okay for your experiments.
The Spec 20 is now blanked.
Remember, the Spec 20 MUST be **re-blanked every time the wavelength is changed**.

The blanks for parts 2, 3, and 4 are **different.**

The Sample

Once the Spec 20 is blanked, you are ready to put the second cuvette containing the sample in (logo front, 2/3-3/4 full, lid closed).
Record its %T to one decimal place.
You should read %T values from the Spec 20 because the scale is linear, allowing estimation between lines, and then convert to absorption, A.
When finished with all measurements, the sample holder should be empty, the cuvettes should be thoroughly washed and put in the rack to dry, and the Spec 20 should be turned off.

Note: If the dial needle flickers or wanders after 5 seconds, let your TA or the stockroom staff know.

Before lab section
1) Use %T data collected for aqueous $FeSCN^{2+}$, $[FeSCN^{2+}]_{eq}$, over a wavelength range in the near-UV and short-wavelength visible regions of the electromagnetic spectrum to calculate *A* at each wavelength, to create a spectral profile plot (*A*. vs. λ), and to determine λ_{max}.
2) Use %T data for known $[FeSCN^{2+}]_{eq}$ to calculate *A* for each concentration, to create a Beer's law plot, and to find the slope of the best fit line (forced through the origin. You will determine an approximate proportionality constant, εb, between *A* and $[FeSCN^{2+}]_{eq}$ and to calculate the value of the molar extinction coefficient, ε, at the λ_{max} for aqueous $FeSCN^{2+}$.

During lab section
3) Volumetrically prepare aqueous equilibrium mixtures of Fe^{3+}, SCN^{-}, and $FeSCN^{2+}$ and measure %T for each solution at λ_{max}.

After lab section using your experimental data
4) Calculate $[Fe^{3+}]_{eq}$, $[SCN^{-}]_{eq}$, and $[FeSCN^{2+}]_{eq}$ from *A* data calculated from %T values obtained experimentally. Find an average $K \pm \sigma_K$, and analyze your results.

Part 1 Spectral profile and λ_{max} of $FeSCN^{2+}$
Before lab section

You will be provided %T data over a wavelength region in the near-UV/visible region of the electromagnetic spectrum. Use this to create your spectral profile for aqueous $FeSCN^{2+}$ and to determine your experimental λ_{max}.

Calculate A from %T at each wavelength. The number of significant figures in %T determines the number of decimal places in A.

$$A = -\log\left(\frac{\%T}{100\%}\right)$$

If %T has three significant figures, A has three decimal places. If %T has two significant figures, A has two decimal places.

Plot A vs. λ (y vs. x) to create a spectral profile.

Determine your experimental λ_{max} and compare it to the literature value of 465 nm.
Answer for experimental λ_{max} _____nm
Difference from theoretical λ_{max} _____nm
%error to 3 sig figs _____%

Why is it important to collect %T data at λ_{max}, rather than at a wavelength with lower absorbance? How would this impact your experimental results?

Part 2. Beer's law for $[FeSCN^{2+}]_{eq}$

Before lab section

You will be provided data to use to determine the proportionality constant, εb, between A and $[FeSCN^{2+}]_{eq}$ and the molar extinction coefficient, ε, for $FeSCN^{2+}$ at λ_{max},.

Calculate A from %T. Plot A vs. $[FeSCN^{2+}]_{eq}$ (y vs. x) to create the Beer's law plot. What trend do you expect the A values to show as $[FeSCN^{2+}]_{eq}$ increases? Should A increase or decrease as $[FeSCN^{2+}]_{eq}$ increases?
Upload plot

Find the slope of the best fit line with the y-intercept forced through (0,0). The best fit line should be straight, and the slope should have a value that is large and positive. See the instructions for Excel or carefully make the graph by hand. Please do not use Google sheets, and please do not use individual data points.

Report the slope to two significant figures and with the correct units.

With $b = 1.00$ cm, calculate ε to two significant figures. Compare your result with the literature value of ε at $\lambda_{max.}$, which has been reported as 4700 L/(mol·cm).

slope $= \varepsilon b$ so $\varepsilon = \frac{\text{slope}}{b}$ _____L/mol
%error _____%

Part 3. *K* for Formation of $[FeSCN^{2+}]_{eq}$: $Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$ *during lab section (and after)*

You need (take in small, labeled beakers):
~15 mL 2.0×10^{-3} *M* NaSCN
~30 mL 2.0×10^{-3} *M* $Fe(NO_3)_3$
~15 mL 2.0×10^{-3} *M* $NaNO_3$

Two cuvettes: one for the blank (see **procedure** and one for the **samples**)

Organize and label your glassware (see procedure below for guidance).

You need only one 10.00-mL volumetric flask to make the solutions using the 2.0×10^{-3} *M* reagents. The volumes of **2.0×10^{-3} *M* NaSCN** (1.00, 2.00, 3.00, 4.00, 5.00 mL) and the volume of **2.0×10^{-3} *M* $Fe(NO_3)_3$** must be volumetrically pipetted. The **2.0×10^{-3} *M* $NaNO_3$** volume is not 10.00 mL $- V_{NaSCN} - V_{Fe(NO_3)_3}$; it is whatever is required to dilute the final volume to 10.00 mL in the 10.00-mL volumetric flask.

As you make each solution, store it in a labeled test tube (6 total; the blank plus 5 solutions). Set up the test tubes and label them before you start.

Make the first solution.

1. Volumetrically pipet **1.00 mL 2.0×10^{-3} *M* NaSCN** into your 10.00-mL volumetric flask. Volumetrically pipet in **5.00 mL 2.0×10^{-3} *M* $Fe(NO_3)_3$** into the flask. Please be **very careful** with the pipet and pipetter.

2. Fill the flask almost to the line around the flask's neck with **2.0×10^{-3} *M* $NaNO_3$**. Use a disposable pipet to add drops of **2.0×10^{-3} *M* $NaNO_3$** until the bottom of the meniscus is on the line around the flask's neck.

3. Insert the stopper, hold the stopper in, and invert the flask several times to mix the solution well. The resulting solution should be the lightest orange-red in color. Store in a labeled test tube.

Prepare the remaining solutions.

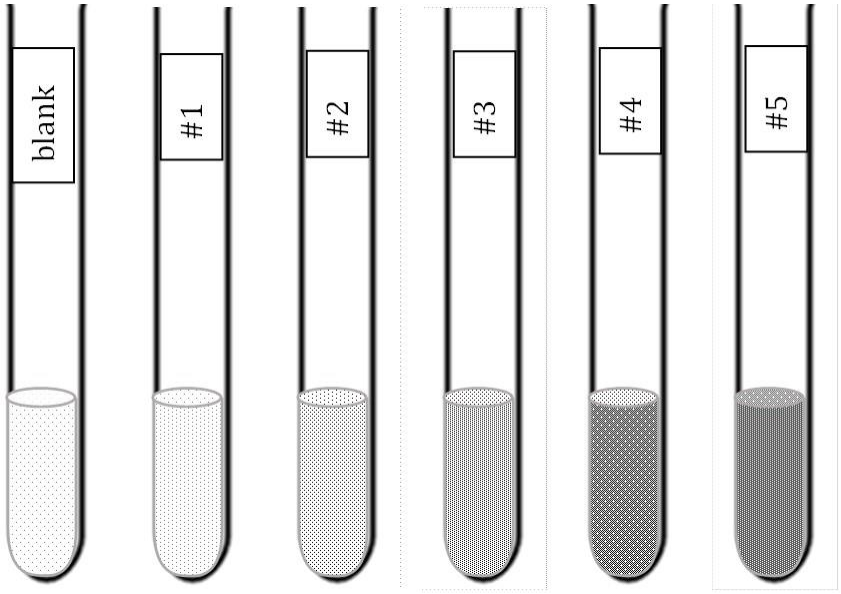
4. Repeat step 1 using volumetrically pipetted **2.00 mL of 2.0×10^{-3} *M* NaSCN** and **5.00 mL 2.0×10^{-3} *M* $Fe(NO_3)_3$**, using **2.0×10^{-3} *M* $NaNO_3$** to dilute to the 10.00-mL mark.

5. Repeat step 1 using volumetrically pipetted **3.00 mL of 2.0×10^{-3} *M* NaSCN** and **5.00 mL 2.0×10^{-3} *M* $Fe(NO_3)_3$**, using **2.0×10^{-3} *M* $NaNO_3$** to dilute to the 10.00-mL mark.

6. Repeat step 1 using volumetrically pipetted **4.00 mL of 2.0×10^{-3} *M* NaSCN** and **5.00 mL 2.0×10^{-3} *M* $Fe(NO_3)_3$**, using **2.0×10^{-3} *M* $NaNO_3$** to dilute to the 10.00-mL mark.

7. Repeat step 1 using volumetrically pipetted **5.00 mL of 2.0×10^{-3} *M* NaSCN** and **5.00 mL 2.0×10^{-3} *M* $Fe(NO_3)_3$**.

8. Make your blank by volumetrically pipetting **5.00 mL of 2.0×10^{-3} *M* $Fe(NO_3)_3$** into your 10.00-mL flask and diluting to the mark with **2.0×10^{-3} *M* $NaNO_3$.**



STOP. You should have 6 solutions in labeled test tubes. As the volume of solution A increases, the orange-red color of the solutions should deepen. The blank should not be orange-red.

9. Once the Spec 20 is available, make sure the Spec 20 is set to λ_{max}. Fill your blank cuvette ~2/3 full with the **part 3 blank.** Fill the sample cuvette ~2/3 full with the most dilute

solution (**1.00 mL** $\mathbf{2.0 \times 10^{-3}}$ ***M*** **NaSCN** and **5.00 mL** $\mathbf{2.0 \times 10^{-3}}$ ***M*** $\mathbf{Fe(NO_3)_3}$ diluted to 10.00 mL with $\mathbf{2.0 \times 10^{-3}}$ ***M*** $\mathbf{NaNO_3}$; labeled blank on the figure).

10. Set 0.0%T (nothing in the sample holder, lid closed, left knob) and 100.0%T (blank in the sample holder, lid closed, right knob). Insert the cuvette containing the first sample and record %T to one decimal place.

11. Repeat steps 9 and 10 with each of the remaining solutions (4,2; 4,3; 4,4; and, 4,5).

12. Please follow your TA's instructions for cleanup and waste disposal.

Make sure that you have thoroughly washed all of your glassware, have returned any equipment/glassware that you borrowed, have two clean cuvettes in the holder by your Spec 20, have turned off your Spec 20, and have wiped down your lab station. Put the disposable pipet you used into a broken glass box, not the trash.

Washing glassware well means tap water and soap, tap water rinses, and a final deionized water rinse.

Make sure you have a **complete set of data** for all parts of the procedure **BEFORE leaving the lab**.

13. *After you have completed the procedure and have cleaned up*, calculate *A* from %T for each sample.

- Calculate $[\mathrm{FeSCN}^{2+}]_{eq}$ to two significant figures.

$$[\mathrm{FeSCN}^{2+}]_{eq} = c = \frac{A}{\varepsilon b}, where\ \varepsilon b = (literature\ value\ of\ \varepsilon\ \times the\ pathlength\ in\ cm)$$

- Calculate the initial SCN^- and Fe^{3+} concentrations to two significant figures.

$$M_{[\mathrm{SCN}^-]_{in}} = \frac{(2.0 \times 10^{-3}\ M\ \mathrm{SCN}^-)(\mathrm{V}^-_{\mathrm{SCN}}\ \text{in mL})}{(10.00\ \text{mL})}$$
$$M_{[\mathrm{Fe}^{3+}]_{in}} = \frac{(2.0 \times 10^{-3}\ M\ \mathrm{Fe}^{3+})(5.00\ \text{mL})}{(10.00\ \text{mL})}$$

15. Calculate the equilibrium concentrations of SCN^- and Fe^{3+}. Use ICE charts to help you.

	Fe^{3+}	+	SCN^-	⇌	FeSCN^{2+}
Initial	$M_{[\mathrm{Fe}^{3+}]_{in}}$		$M_{[\mathrm{SCN}^-]_{in}}$		0

Change	$-c$	$-c$	$+c$
Equilbrium	$M_{[\mathrm{Fe^{3+}}]_{in}} - c$	$M_{[\mathrm{SCN^-}]_{in}} - c$	$c = \frac{A}{slope}$

ICE table for sample 2

	$\mathrm{Fe^{3+}(aq)}$ +	$\mathrm{SCN^-(aq)}$ ⇌	$\mathrm{FeSCN^{2+}(aq)}$
Initial	$[\mathrm{Fe^{3+}}]_{in}$	$[\mathrm{SCN^-}]_{in}$	0
Change	$-c$	$-c$	$+c$
Equilibrium	$[\mathrm{Fe^{3+}}]_{in} - c$	$[\mathrm{SCN^-}]_{in} - c$	$c = [\mathrm{FeSCN^{2+}}]_{eq} = \frac{A}{\varepsilon b}$

ICE table for sample 3

	$\mathrm{Fe^{3+}(aq)}$ +	$\mathrm{SCN^-(aq)}$ ⇌	$\mathrm{FeSCN^{2+}(aq)}$
Initial	$[\mathrm{Fe^{3+}}]_{in}$	$[\mathrm{SCN^-}]_{in}$	0
Change	$-c$	$-c$	$+c$
Equilibrium	$[\mathrm{Fe^{3+}}]_{in} - c$	$[\mathrm{SCN^-}]_{in} - c$	$c = [\mathrm{FeSCN^{2+}}]_{eq} = \frac{A}{\varepsilon b}$

ICE table for sample 4

	$\mathrm{Fe^{3+}(aq)}$ +	$\mathrm{SCN^-(aq)}$ ⇌	$\mathrm{FeSCN^{2+}(aq)}$
Initial	$[\mathrm{Fe^{3+}}]_{in}$	$[\mathrm{SCN^-}]_{in}$	0
Change	$-c$	$-c$	$+c$
Equilibrium	$[\mathrm{Fe^{3+}}]_{in} - c$	$[\mathrm{SCN^-}]_{in} - c$	$c = [\mathrm{FeSCN^{2+}}]_{eq} = \frac{A}{\varepsilon b}$

ICE table for sample 5

	$\mathrm{Fe^{3+}(aq)}$ +	$\mathrm{SCN^-(aq)}$ ⇌	$\mathrm{FeSCN^{2+}(aq)}$
Initial	$[\mathrm{Fe^{3+}}]_{in}$	$[\mathrm{SCN^-}]_{in}$	0
Change	$-c$	$-c$	$+c$
Equilibrium	$[\mathrm{Fe^{3+}}]_{in} - c$	$[\mathrm{SCN^-}]_{in} - c$	$c = [\mathrm{FeSCN^{2+}}]_{eq} = \frac{A}{\varepsilon b}$

ICE table for sample 6

	$\mathrm{Fe^{3+}(aq)}$ +	$\mathrm{SCN^-(aq)}$ ⇌	$\mathrm{FeSCN^{2+}(aq)}$
Initial	$[\mathrm{Fe^{3+}}]_{in}$	$[\mathrm{SCN^-}]_{in}$	0
Change	$-c$	$-c$	$+c$
Equilibrium	$[\mathrm{Fe^{3+}}]_{in} - c$	$[\mathrm{SCN^-}]_{in} - c$	$c = [\mathrm{FeSCN^{2+}}]_{eq} = \frac{A}{\varepsilon b}$

16. Calculate K for each solution to two significant figures.

$$K = \frac{[\mathrm{FeSCN}^{2+}]_{eq}}{[\mathrm{Fe}^{3+}]_{eq}[\mathrm{SCN}^{-}]_{eq}} = \frac{c}{([\mathrm{Fe}^{3+}]_{in} - c)([\mathrm{SCN}^{-}]_{in} - c)}, \text{where } c = \frac{A}{\varepsilon b}$$

17. Calculate the unrounded value of average K and its standard deviation, $K \pm \sigma_K$; then, round to the correct number of significant figures.

How does your average K compare to the literature value, which has been reported as 890. Note: different sources report different values for K but all are in the hundreds.

Do your data support that K is a constant at a given temperature (how large is your σ_K relative to K)? Should σ_K be large or small, particularly in relation to the value of K?

Results / Sample Calculations

λ_{max}
slope of the Beer's law plot, εb, and molar extinction coefficient, ε, at λ_{max}
$K \pm \sigma_K$

Complete the online inlab or write a lab report as directed by your TA.

Discussion Questions and Review Topics

What did you do and what did you find?
What were the primary sources of error?
How close was your experimental λ_{max} to the literature value? ε? K? How "constant" is K at room temperature (σ_K relative to K)?
How could the accuracy and precision of the results be improved? What conclusions can you draw about the experimental method and your results?