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 endo- or exothermicity of the forward reaction, which is reflected in how the value of the equilibrium constant *K* changes as a function of temperature, will be investigated qualitatively. The value of *K* at room temperature will be calculated from equilibrium concentrations derived from measurements made by absorption spectroscopy.

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.
Apply linear fitting methods to find relationships between dependent and independent variables, such as percent transmittance (absorbance) and concentration.
Explain and apply Beer's Law; describe the assumptions and limitations imposed by the nature of the equilibrium on the calculation of $FeSCN^{2+}$ associated with the absorption data.
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.
Analyze, quantify, and discuss the uncertainty in results when assumptions are used.

Suggested Review and External Reading

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

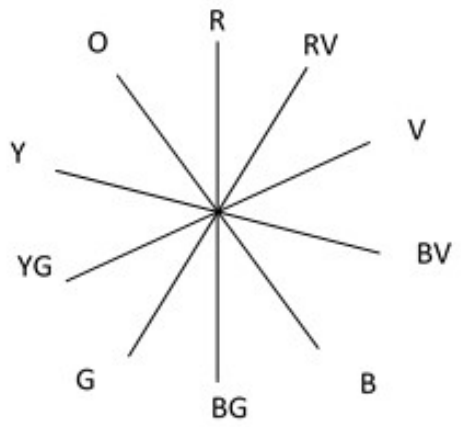
Introduction

This experiment investigates the equilibrium established by the reaction in aqueous solution of iron (III) ions, Fe^{3+}, with thiocyanate ions, SCN^-, including the endo- or exothermicity of the forward reaction 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 darkness 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}).

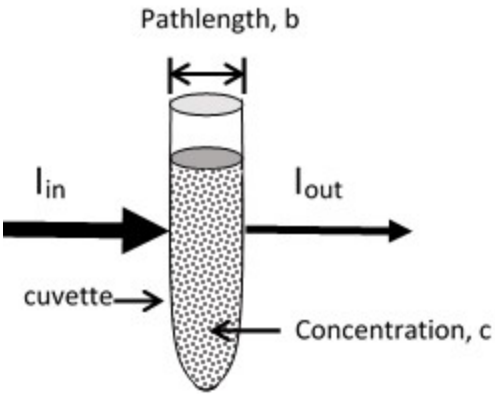


Complementary colors are on opposite sides of the color wheel. When complementary colors are mixed, white light is the result.

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.

Using aqueous $Fe(NO_3)_3$ and NaSCN with appropriately chosen initial concentrations can produce solutions in which $[FeSCN^{2+}]_{eq}$ can be approximated with some confidence. If $[Fe^{3+}]_{in}$ is much greater than $[SCN^{-}]_{in}$, then it might be reasonable to assume that

essentially all of the SCN^- initially present reacts to produce $FeSCN^{2+}$ at equilibrium. $[Fe^{3+}]_{in}$ remains roughly unchanged because it is present in very large excess.

$[SCN^-]_{in} \rightarrow [FeSCN^{2+}]_{eq}$ and $[Fe^{3+}]_{in} \approx [Fe^{3+}]_{eq}$

$$Q = \frac{0}{[Fe^{3+}]_{in}[SCN^-]_{in}} \rightarrow K = \frac{[FeSCN^{2+}]_{eq}}{[Fe^{3+}]_{eq}[SCN^-]_{eq}} \xrightarrow{[Fe^{3+}]_{in} \gg [SCN^-]_{in}} \frac{([FeSCN^{2+}]_{eq} \approx [SCN^-]_{in})}{([Fe^{3+}]_{in})([SCN^-]_{eq} \rightarrow 0)}$$

The value of the ratio of $[FeSCN^{2+}]_{eq}$ to $[SCN^-]_{eq}$ provides insight into the validity of this approximation. The larger its value, the "better" the assumption – very little of the initial SCN^- remains uncombined; most has reacted and is present as $FeSCN^{2+}$ at equilibrium. This is consistent with a large K value and an equilibrium position that favors products.

$$\frac{[FeSCN^{2+}]_{eq}}{[SCN^-]_{eq}} = \frac{K \cdot [Fe^{3+}]_{eq}}{1} \approx \frac{K \cdot [Fe^{3+}]_{in}}{1}$$

Once the proportionality between A and $[FeSCN^{2+}]_{eq}$ has been determined, 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
Parts 1, 2, and 4 only - iron (III) nitrate solution, 2.0×10^{-3} M $Fe(NO_3)_3$
Part 3 only - solution B, iron (III) nitrate solution, 0.010 M $Fe(NO_3)_3$

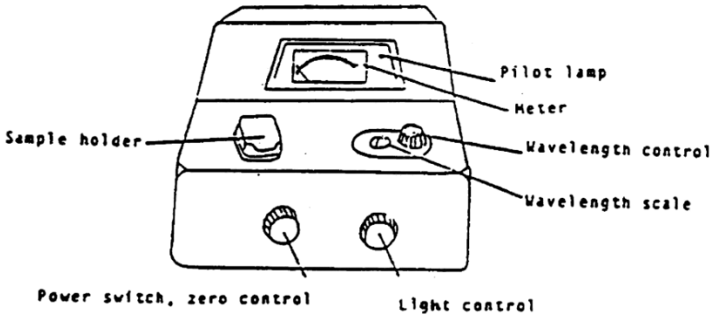
Caution

Read the labels on the reagent bottles carefully. Label all glassware.
There are two $Fe(NO_3)_3$ solutions. One is 500 times more concentrated than the other.
Using the wrong $Fe(NO_3)_3$ solution will not lead to good data.
$Fe(NO_3)_3$ solutions are acidic. Please be careful. Wash your hands frequently. Inform your TA in the event of a spill.

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.

Teamwork

You may be asked to work with another pair of students in a group of 4. If this is the case, each of you may be put in charge of a given part of the experiment. This does **not** mean that you can focus solely on your section of the procedure.

You must help the other members of your team with their parts of the experiment, just as you would expect them to help you.

You **cannot** leave before your team is finished with the entire experiment or before you have a complete set of data for all four parts of the procedure.

You will be assessed on your cooperation and collaboration with your team, and your grade will reflect how you work together.

Procedure

Lab bench organization: it is strongly recommended that you organize and label your reagents, glassware, and equipment before starting the experiment.

Always take reagents in small labeled beakers, and do not take more than you need. Never pipet out of reagent bottles.

Your group needs only two cuvettes – one for the blank and one for the sample. You must use the same Spec 20 for the entire experiment.

You will:

1) Determine whether the forward reaction is endo- or exothermic.
2) Find λ_{max} for $FeSCN^{2+}$ from its spectral profile.
3) Determine the proportionality constant, εb, between A and $[FeSCN^{2+}]_{eq}$ in Beer's law.
4) Calculate K from concentrations based on $[FeSCN^{2+}]_{eq}$ values calculated from A data.

Part 1 Qualitative observation/endo- or exothermic forward reaction

$\sim$8 mL 2.0×10^{-3} M NaSCN
$\sim$10 mL 2.0×10^{-3} M $Fe(NO_3)_3$
$\sim$2 mL 2.0×10^{-3} M $NaNO_3$
Three large labeled test tubes (+ one cuvette for sample, part 2)

1. Use a 10.00-mL graduated cylinder to add the following volumes of reagents to a small labeled beaker (or labeled 100.0-mL graduated cylinder): 2 mL 2.0×10^{-3} M $NaNO_3$, 8 mL 2.0×10^{-3} M NaSCN, and 10 mL 2.0×10^{-3} M $Fe(NO_3)_3$.

2. Pour enough of the solution from step 1 to fill a Spec 20 cuvette approximately 2/3 full (no more than 3/4 full) for part 2. Split the remaining solution between three large labeled test tubes.

3. Place one test tube in an ice bath and one in the warm water bath for at least 10 minutes (the time does not have to be exact but it should be no less than 10 minutes).

4. Compare the color of the three solutions (ice, room, and warm temperatures). Which solution is the deepest orange-red? What does mean in terms of the relative $[FeSCN^{2+}]_{eq}$ in each solution? What does this imply about the effect of temperature on the value of *K*? Is the forward reaction endo- or exothermic (it may be helpful to think about Le Châtelier's principle)?

Part 2 Spectral profile and λ_{max} of $FeSCN^{2+}$

Two cuvettes: one for the blank (**2.0×10^{-3} *M* $NaNO_3$**) and one for the sample (**prepared in part 1**)

5. Measure the inner diameter of the cuvette in cm to two decimal places.

6. Fill your second cuvette 2/3 full with 2.0×10^{-3} *M* $NaNO_3$. This is the blank.

%T data should be recorded to one decimal place at the following wavelength intervals:

10-nm intervals: 370 – 450 nm
5-nm intervals: 450 – 480 nm
10-nm intervals: 480 – 560 nm

7. Set the wavelength on the Spec 20. Use the left knob to set 0.0 %T while the sample holder is empty and the lid is closed. Insert the cuvette containing the blank into the sample holder and close the lid. Use the right know to set 100.0 %T. Insert the cuvette containing the solution prepared in part 1 (the sample) into the sample holder and close the lid. Record the %T to one decimal place.

8. Repeat step 7 at the next wavelength.

9. Set the Spec 20 to λ_{max}, the wavelength with the lowest %T reading.

10. *When done with the experiment*, calculate *A* from %T at each wavelength. 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.

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

Part 3. Beer's law for $[FeSCN^{2+}]_{eq}$

$\sim$ 5 mL 2.0×10^{-3} *M* NaSCN
$\sim$80 mL 0.10 *M* $Fe(NO_3)_3$ = solution B

NO 2.0×10^{-3} *M* $Fe(NO_3)_3$ or 2.0×10^{-3} *M* $NaNO_3$

Two cuvettes: one for the blank (**0.10 *M* $Fe(NO_3)_3$** = solution B and one for the **samples**)

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

You need one 50.00-mL volumetric flask to prepare solution A and one 10.00-mL volumetric flask to make the remaining solutions, which are dilutions of solution A (1.00, 3.00, 5.00, 7.00, 9.00 mL of A diluted to 10.00 mL with solution B).

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

You will prepare solution A, the most concentrated $FeSCN^{2+}$ solution first in a 50.00-mL volumetric flask. You should store some of this solution A in a labeled test tube for a %T measurement once the Spec 20 is available (and when you are ready to do all of the part 3 solutions at one time.

The remaining solutions for which you will measure %T will be dilutions of solution A. You will use 0.10 *M* $Fe(NO_3)_3$ to dilute known volumes of solution A to a final volume of 10.00 mL. You need only ONE 10.00-mL volumetric flask. You will make each solution and store it in a labeled test tube until the Spec 20 is available.

Recall you are using a large excess of Fe^{3+} so that you can assume $[FeSCN^{2+}]_{eq} \approx [SCN^-]_{in}$.

Once you have actually determined *K*; you must return to this assumption and verify its validity.

Caution

Incorrect use of the pipet and pipetter can result in **serious injury**.
Please **do NOT force or jam the pipet** into the pipetter.
If you push too hard, the pipet can break and **cut your hand**.
Use **just enough force** to create a seal. The pipet does not "click" into place.
Hold both the pipet and pipetter at all times.
If you pull any solution into the pipetter, please give it to your TA so that it can be cleaned.

If you have trouble, **ask your TA for help**.

12. Obtain your reagents, each in a small labeled beaker. You need only **$\sim$ 5 mL of 2.0×10^{-3} *M* NaSCN and $\sim$80 mL of 0.10 *M* $Fe(NO_3)_3$ = solution B**.

Prepare solution A, the most concentrated $FeSCN^{2+}$ solution.

13. Volumetrically pipet **5.00 mL 2.0×10^{-3} *M* NaSCN** into a 50.00-mL volumetric flask.

14. Fill the flask almost to the line around the flask's neck with **0.10 *M* $Fe(NO_3)_3$ = solution B**. Use a disposable pipet to add drops of **0.10 *M* $Fe(NO_3)_3$ = solution B** until the bottom of the meniscus is on the line around the flask's neck.

15. Insert the stopper, hold the stopper in, and invert the flask several times to mix the solution well. The resulting solution is solution A.

From solution A, prepare the remaining $FeSCN^{2+}$ solutions.

16. Using your 1.00-mL volumetric pipet, add 1.00 mL of **solution A** to your 10.00-mL volumetric flask (you need only one of these – wash it out between each solution you prepare). Dilute and mix as you did in step 14 using **0.10 *M* $Fe(NO_3)_3$ = solution B**.

Pour the solution into a large labeled test tube.

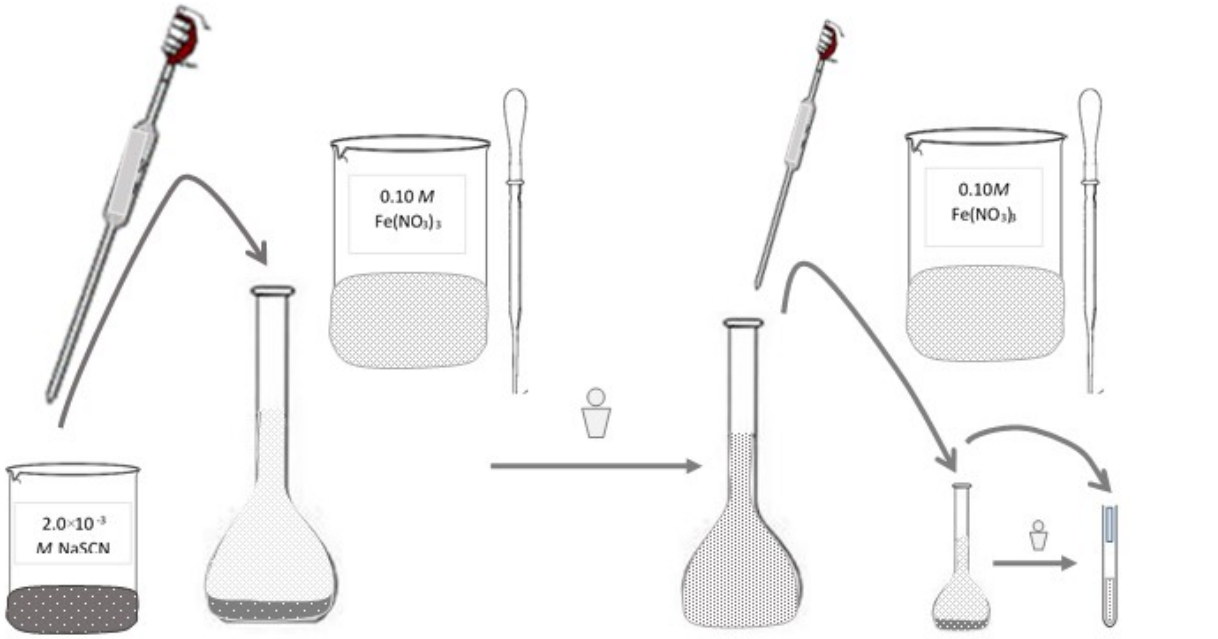
17. Repeat step 16 using 3.00 mL of **solution A**.

18. Repeat step 16 using 5.00 mL of **solution A**.

19. Repeat step 16 using 7.00 mL of **solution A**.

20. Repeat step 16 using 9.00 mL of **solution A**.

21. Pour $\sim$10 mL of **solution A** into a large labeled test tube; this is the most concentrated orange-red solution.

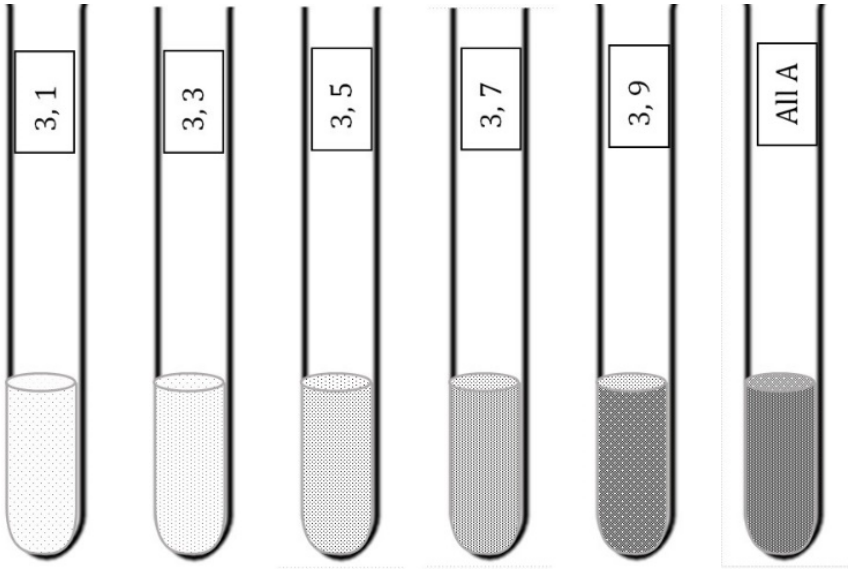


Solution A prep: volumetrically pipet 5.00 mL 2.0×10^{-3} *M* NaSCN → 50.00-mL volumetric flask & dilute to mark with 0.10 *M* $Fe(NO_3)_3$ = Solution B.

Stopper and mix well.

Dilutions of A: volumetrically pipet # mL Solution A → 10.00-mL volumetric flask & dilute to mark with 0.10 *M* $Fe(NO_3)_3$ = Solution B.

Stopper and mix well. Store in labeled test tube.



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.

22. Once the Spec 20 is available, fill your blank cuvette ~2/3 full with $\mathbf{0.10\ \mathit{M}\ Fe(NO_3)_3}$ = **solution B.** Fill the sample cuvette ~2/3 full with the most dilute solution (**1.00 mL solution A diluted to 10.00 mL with solution B**; labeled 3,1 on the figure).

23. Make sure the Spec 20 is set to λ_{max}. 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.

24. Repeat steps 22 and 23 with each of the remaining solutions (3,3; 3,5; 3,7; 3,9; and, pure A). Make sure to measure the inner diameter of the sample cuvette in cm to two decimal places.

25. *When done with the experiment*, calculate $M_{[SCN^-]_{in}} = M_{[FeSCN^{2+}]_{eq}}$ to two significant figures A from %T for each sample and calculate . Plot A vs. $[FeSCN^{2+}]_{eq} \approx [SCN^-]_{in}$ (y vs. x) to create the Beer's law plot. The best-fit line should be straight with a slope equal to εb; the y-intercept should be forced through (0,0).

$$In\ solution\ A\text{:}\ M_{[SCN^-]_{in}} = M_{[FeSCN^{2+}]_{eq}} = \frac{(2.0 \times 10^{-3}\ M\ SCN^-)(5.00\ mL)}{(50.00\ mL)}$$

$$In\ dilutions\ of\ A\text{:}\ M_{[SCN^-]_{in}} = M_{[FeSCN^{2+}]_{eq}} = \frac{(M\ A)(V_A)}{(10.00\ mL)} = \frac{(2.0 \times 10^{-4}\ M\ SCN^-)(V_A)}{(10.00\ mL)}$$

$$A = -\log\left(\frac{\%T}{100\%}\right) = \varepsilon bc = \varepsilon b[FeSCN^{2+}]_{eq}$$

26. Find the slope of the best fit line to two decimal places (do not use individual data points). See the instructions for Excel or Google Sheets, or carefully make the graph by hand and find the slope. The value should be large.

27. Calculate ε, the molar extinction coefficient, to two decimal places.

$$\text{slope} = \varepsilon b \text{ so } \varepsilon = \frac{\text{slope}}{b}$$

You will check and analyze the assumption regarding $[FeSCN^{2+}]_{eq}$ once you have determined K (part 4).

Part 4. K for Formation of $[FeSCN^{2+}]_{eq}$: $Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$

~15 mL $\mathbf{2.0 \times 10^{-3}\ \mathit{M}}$ NaSCN

~30 mL 2.0×10^{-3} *M* $Fe(NO_3)_3$
~15 mL 2.0×10^{-3} *M* $NaNO_3$

NO 0.10 *M* $Fe(NO_3)_3$ = solution B

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

28. 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.

29. 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.

30. 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.

31. 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.

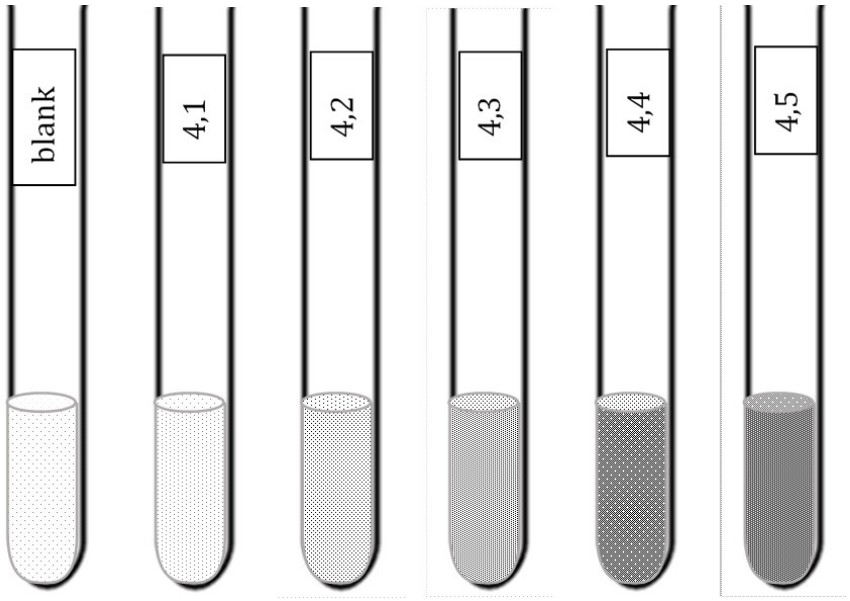
32. Repeat step 29 using volumetrically pipetted **2.00 mL of 2.0×10^{-3} *M* NaSCN** and **5.00 mL 2.0×10^{-3} *M* $Fe(NO_3)_3$**, using **2.0×10^{-3} *M* $NaNO_3$** to dilute to the 10.00-mL mark.

33. Repeat step 29 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.

34. Repeat step 29 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.

35. Repeat step 29 using volumetrically pipetted **5.00 mL of 2.0×10^{-3} *M* NaSCN** and **5.00 mL 2.0×10^{-3} *M* $Fe(NO_3)_3$**.

36. 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.

37. Once the Spec 20 is available, fill your blank cuvette ~2/3 full with the **part 4 blank.** Fill the sample cuvette ~2/3 full with the most dilute solution (**1.00 mL 2.0×10^{-3} *M* NaSCN** and **5.00 mL 2.0×10^{-3} *M* $Fe(NO_3)_3$** diluted to 10.00 mL with **2.0×10^{-3} *M* $NaNO_3$**; labeled 4,1 on the figure).

38. Make sure the Spec 20 is set to λ_{max}. 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.

39. Repeat steps 37 and 38 with each of the remaining solutions (4,2; 4,3; 4,4; and, 4,5).

40. *When done with the experiment*, calculate *A* from %T for each sample. Calculate $[\mathrm{FeSCN}^{2+}]_{eq}$ to two significant figures.

$$[\mathrm{FeSCN}^{2+}]_{eq} = c = \frac{A}{\varepsilon b} = \frac{A}{\text{slope, part 3}}$$

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

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

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

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

43. Calculate *K* for each solution to two significant figures.

$$K = \frac{[\mathrm{FeSCN}^{2+}]_{eq}}{[\mathrm{Fe}^{3+}]_{eq}[\mathrm{SCN}^-]_{eq}} = \frac{c}{(M_{[\mathrm{Fe}^{3+}]_{in}} - c)(M_{[\mathrm{SCN}^-]_{in}} - c0}$$

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

45. Check the assumption you made in part 3. First, calculate the ratio of $[\mathrm{FeSCN}^{2+}]_{eq}$ to $[\mathrm{SCN}^-]_{eq}$.

Recall that a large excess of Fe^{3+} was used so that you could approximate the equilibrium concentration of FeSCN^{2+} to be roughly equal to initial SCN^- molarity: $[\mathrm{FeSCN}^{2+}]_{eq} \approx [\mathrm{SCN}^-]_{in}$. You further assumed that the Fe^{3+} concentration remained essentially unchanged: $[\mathrm{Fe}^{3+}]_{eq} \approx 0.10\ M$.

$$K = \frac{[\mathrm{FeSCN}^{2+}]_{eq}}{[\mathrm{Fe}^{3+}]_{eq}[\mathrm{SCN}^{-}]_{eq}} \xrightarrow{[\mathrm{Fe}^{3+}]_{in} \gg [\mathrm{SCN}^{-}]_{in}} \frac{([\mathrm{FeSCN}^{2+}]_{eq} \approx [\mathrm{SCN}^{-}]_{in})}{(0.10)([\mathrm{SCN}^{-}]_{eq} \to 0)}$$

$$\frac{[\mathrm{FeSCN}^{2+}]_{eq}}{[\mathrm{SCN}^{-}]_{eq}} = \frac{K \cdot [\mathrm{Fe}^{3+}]_{eq}}{1} \approx \frac{K \cdot (0.10)}{1}$$

Second, interpret the ratio. What percentage of the initial SCN^{-} was combined with Fe^{3+} at equilibrium? What percentage remains unreacted? To help you, here is an example. Suppose K = 350.

$$\frac{[\mathrm{FeSCN}^{2+}]_{eq}}{[\mathrm{SCN}^{-}]_{eq}} = \frac{K \cdot [\mathrm{Fe}^{3+}]_{eq}}{1} \approx \frac{K \cdot (0.10)}{1} = \frac{350 \cdot (0.10)}{1} = \frac{35}{1}$$

This means that, for every $35 + 1 = 36$ initial SCN^{-}, 35 are combined with Fe^{3+} and present as FeSCN^{2+} at equilibrium. The percent combined and uncombined can be determined.

$$\%\mathrm{SCN}^{-} \text{ present as } \mathrm{FeSCN}^{2+} \text{at equilibrium} = \frac{35}{36} \times 100\% = 97\%$$

$$\%\mathrm{SCN}^{-} \text{ uncombined at equilibrium} = \frac{1}{36} \times 100\% = 100\% - 97\% = 3\%$$

You might expect a standard deviation in K due to just this approximation to be $\sim 3 \times 3\% = 9\% = 30$; $3 \times 3\%$ because $[\mathrm{FeSCN}^{2+}]_{eq} = c$ was used to find not only $[\mathrm{FeSCN}^{2+}]_{eq}$ but also two more equilibrium concentrations, $[\mathrm{Fe}^{3+}]_{eq}$ and $([\mathrm{SCN}^{-}]_{eq}$. How does your σ_K compare to this estimate? What does this suggest about other experimental sources of error?

46. 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.

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

Results / Sample Calculations

Endo- or exothermic forward reaction?
λ_{max} and ε
$K \pm \sigma_K$

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?
What was the value of $\frac{[\mathrm{FeSCN}^{2+}]_{eq}}{[\mathrm{SCN}^{-}]_{eq}}$ and how does this reflect the "goodness" of your experimental *K*?
How could the accuracy of the results be improved? What conclusions can you draw about the experimental method and your results?