

Experiment 8: DETERMINATION OF AN EQUILIBRIUM CONSTANT

Purpose: The equilibrium constant for the formation of iron(III) thiocyanate complex ion is to be determined.

Introduction: In the previous week, we qualitatively investigated how an equilibrium shifts in response to a stress to re-establish equilibrium. This week we will quantitatively assess the equilibrium constant for the same reaction: the reaction of iron(III) cation complexing with a thiocyanate anion (SCN^-) to form the iron(III) thiocyanate complex, $\text{Fe}(\text{SCN})^{2+}$ (Equation 1). Its equilibrium expression is as shown in Equation 2.



$$K_{\text{eq}} = \frac{[\text{Fe}(\text{SCN})^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} \quad \text{Equation 2}$$

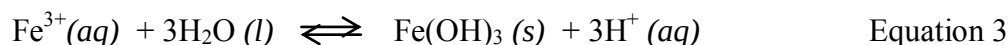
If K_{eq} is a large number (>1), then the chemical equilibrium favors the formation of product (large numerator). If K_{eq} is a small number (<1) then the chemical equilibrium favors the formation of reactants (large denominator). In this experiment, several solutions of varying initial concentrations of the reactants are to be prepared. Despite the different concentrations, the equilibrium constants calculated from their equilibrium concentrations should be the same, as long as the temperature is kept constant.

Before we begin the study of the equilibrium concentrations, we must first prepare a standard curve to help us determine the concentration of $\text{Fe}(\text{SCN})^{2+}$ at equilibrium. Le Châtelier's Principle states that if at equilibrium a change is applied to a system, the species will react to offset the change so as to maintain the equilibrium. We will use this principle to aid in the preparation of the standard curve. It will be made by plotting the absorbance *versus* concentration of the red iron(III) thiocyanate complex, $\text{Fe}(\text{SCN})^{2+}$. If the concentration of the reactant, iron(III) nitrate, is increased (0.200 M), so as to become much larger than the thiocyanate anion concentration (0.00200M), then the reaction (Equation 1) will be forced almost completely to products. In this situation, the iron(III) concentration is 100 times that of the thiocyanate, therefore essentially all the SCN^- anions will react to produce the red colored product, $\text{Fe}(\text{SCN})^{2+}$. Thus, within the limits of our detection apparatus, the final concentration of $\text{Fe}(\text{SCN})^{2+}$ is equal to the initial concentration of SCN^- . The intensity of the red color will be measured spectrophotometrically and will be directly proportional to the equilibrium concentration of the $\text{Fe}(\text{SCN})^{2+}$ species. (Review Beer's Law from Experiment 3.)

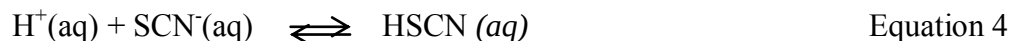
After a standard curve is produced, the conditions will be altered so that the concentrations of each of the two reacting species (Fe^{3+} and SCN^-) will be the same order of magnitude (~ 0.00200 M each). Because the concentrations will be so similar, the system will no longer be forced all the way to the right (towards the products) and you will be able to determine an equilibrium constant from the data. The concentration of $\text{Fe}(\text{SCN})^{2+}$ at equilibrium will be determined spectrophotometrically according to its absorbance in the standard curve. Since for every mole of the red complex, $\text{Fe}(\text{SCN})^{2+}$ produced, one mole of Fe^{3+} and one mole of

SCN^- will have reacted, the equilibrium concentrations (unreacted species) of Fe^{3+} and SCN^- can be determined by subtracting the concentration of $\text{Fe}(\text{SCN})^{2+}$ formed from the initial concentrations before the reaction took place. We can set up an “ICE” table, find the equilibrium concentrations for each of the three species, and solve for K_{eq} .

Each of the initial solutions will be made up so as to contain 0.500 M H^+ . Therefore when mixing the solution of 0.00200 M Fe^{3+} made up in 0.500 M H^+ and the solution of 0.00200 M SCN^- made up in 0.500 M H^+ , no matter what the proportions, the 0.500 M H^+ concentration will be constant. The reason for this is that the iron(III) thiocyanate formation reaction must be run around 0.5 M acid to prevent significant iron hydrolysis (Equation 3) that affects the concentration of iron(III) ions.



Also, the reaction must be run at acid concentration below 0.7 M because otherwise the acid reacts with the thiocyanate reducing the available SCN^- as well (Equation 4).



Each reagent is labeled with its concentration. However, once you mix reagents together, you will have diluted the concentration. The calculations that you use will need to account for these dilutions. An example is below:

Example 1: If 5.08 mL of 0.00200 M $\text{Fe}(\text{NO}_3)_3$ is mixed with 3.10 mL of 0.00200M KSCN and 2.00 mL of 0.500 M HNO_3 , what is the final concentration of the Fe^{3+} ion?

$$\begin{aligned} M_1V_1 &= M_2V_2 \text{ where } V_2 \text{ is the TOTAL volume in the final solution} \\ M_2 &= \frac{M_1V_1}{V_2} = \frac{(0.00200 \text{ M Fe}(\text{NO}_3)_3)(5.08 \text{ mL})}{10.18 \text{ mL}} = 0.000998 \text{ M Fe}(\text{NO}_3)_3 \\ &= 9.98 \times 10^{-4} \text{ M Fe}^{3+} \end{aligned}$$

Check: Is the answer reasonable? M_2 should be more dilute than M_1 .

ICE Table Construction:

ICE tables are useful tables that summarize what is occurring in an equilibrium reaction. The use of ICE tables should have been covered in your lecture class. You need to know that “I” stands for initial concentration of each species in the solution, before they are allowed to react. “C” stands for the change in concentration of each species from the initial concentrations to the equilibrium concentrations. And the “E” stands for equilibrium concentration of each species (i.e. concentration after the reaction has reached equilibrium). Below is an example of how the ICE table will be used.

Example 2: Assume an initial concentration of $[\text{Fe}^{3+}] = 0.00100 \text{ M}$ and an initial concentration of $[\text{SCN}^-] = 0.000600 \text{ M}$ in a sample solution for which you are to determine the concentration of $\text{Fe}(\text{SCN})^{2+}$ from the standard curve. You can set up an ICE table as shown below:

Species	Fe^{3+}	SCN^-	$\text{Fe}(\text{SCN})^{2+}$
I. (Initial)	0.00100 M	0.000600 M	0.00 M
C.(Change)	- X	- X	+ X
E.(Equilibrium)	0.00100 M - X	0.000600 M - X	X

$X = [\text{Fe}(\text{SCN})^{2+}]$ and is to be determined from the standard curve. You can then calculate the equilibrium constant, K_{eq} , using the equilibrium concentrations.

In your ICE tables on the Calculations & Results Page, do not write “X” but use the actual concentration obtained from the standard curve. For example, if $X = 0.000211 \text{ M}$, $[\text{Fe}^{3+}]$ at equilibrium would be $(0.00100 - 0.000211) \text{ M} = 0.00079 \text{ M}$.

Species	Fe^{3+}	SCN^-	$\text{Fe}(\text{SCN})^{2+}$
I. (Initial)	0.00100 M	0.000600 M	0.00 M
C.(Change)	- 0.000211	- 0.000211	+ 0.000211
E.(Equilibrium)	0.00079	0.00039	0.000211

Use of the Standard Curve

The standard curve is a plot of Absorbance *versus* $[\text{Fe}(\text{SCN})^{2+}]$ (Figure 8.1). It can be used to give us the concentration of a solution when given the absorbance. We can either read it off the graph visually or calculate the concentration from the trendline equation. Remember that Beer’s Law indicates the relationship between the concentration and the absorbance is linear. Thus $A = mC + b$ where A is the absorbance, m is the slope, C is the concentration and b is the y-intercept. Considering that A has no units and C has units of M , what is the unit of the slope? What is the unit of the y-intercept? *You should know the answers.*

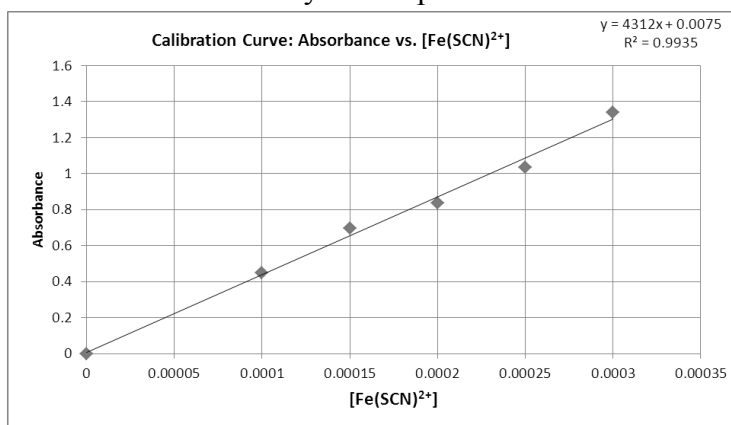


Figure 8.1

For example, the trendline equation from the curve in Figure 8.1 is $y = 4312x + 0.0075$. If an unknown concentration of $\text{Fe}(\text{SCN})^{2+}$ has an absorbance reading of 0.250 then you can solve for the concentration of the $\text{Fe}(\text{SCN})^{2+}$: $y = 4312x + 0.0075$ translates into

$$A = 4312\text{M}^{-1} [\text{FeSCN}^{2+}] + 0.0075$$

$$[\text{FeSCN}^{2+}] = \frac{A - 0.0075}{4312\text{M}^{-1}} \quad \text{and substituting } A = 0.250$$

$$[\text{FeSCN}^{2+}] = \frac{0.250 - 0.0075}{4312\text{M}^{-1}} = \frac{0.2425}{4312\text{M}^{-1}} = 5.62 \times 10^{-5} \text{ M}$$

Procedure: *Work with one partner.*

Setting up the Four Burets:

Do not share buret stands and do not set up burets too close to each other. You do not want to be bumping elbows with each other.

Students will work in pairs but each pair will need to dispense four different solutions by buret. We don't have enough burets to distribute four to each pair of students. Besides it would be a waste of chemicals if an arrangement is not made to share burets. This is how it will be done:

Students first pair up for the experiment. Each pair then selects another pair of students with whom to share burets. For each group of four students, there should be a total of four burets. Each student in the group is to be responsible for cleaning and setting up one buret that the rest of the group will be using:

0.200 M $\text{Fe}(\text{NO}_3)_3$ 0.00200 M KSCN 0.5 M HNO_3 0.00200 M $\text{Fe}(\text{NO}_3)_3$

You must learn not to waste chemicals by taking too much from the stock bottle. As usual you should not be returning extra chemicals to the stock bottle. The **Total Volume** shown in the table below is for each team of 4:

Reagent	Vol for Standard Curve	Vol for Equilibrium Data	Vol per pair of students	Vol per team of 4 students	Vol for Rinse	Total Volume
0.200 M $\text{Fe}(\text{NO}_3)_3$	5 x 2.50 mL	+ 0 mL	12.50 mL	= 12.50 x 2 = 25 mL	+20 mL	45 mL
0.00200 M KSCN	5.00 mL	+ 15.00 mL	20.00 mL	20.00x2 = 40 mL	+ 20 mL	60 mL
0.500 M HNO_3	32.50 mL	+10.00 mL	42.5 mL	42.5x2 = 85 mL	+ 20 mL	105 mL
0.00200 M $\text{Fe}(\text{NO}_3)_3$	none	5x5.00 mL	25 mL	25x2 = 50 mL	+ 20 mL	70 mL

You should know how to do this kind of estimation. STUDY the calculations shown above.

This is what EACH STUDENT has to do with the reagent assigned to him/her:

- Obtain the **Total Volume** (see table above) of the reagent assigned to you in a clean and dry beaker.
- Obtain a buret and rinse it twice with about 10 mL each with the reagent.
- Label a 400-mL beaker as "Waste."
- Fill the buret with only the amount needed by your group of four. Check with your instructor as to how much is needed.
- Make sure you get rid of the air bubble at the tip of the buret.
- Label the buret with the concentration and the formula of the solute with the index card provided.

- At each buret there should be a 50-mL “refill” beaker labeled the same way as the buret to be used if the buret needs refilling.
- You are not responsible for dispensing your reagent for everyone.

In the experiment, each pair of students will then work on the rest of the experiment independent of the other pair, measuring out solutions and obtaining absorbance values.

At the end of the experiment, each student will then clean up the buret he/she had set up initially. However, check to make sure the buret is no longer needed by the other students in the group before cleaning up. Slow workers may end up having to clean up all 4 burets. FOLLOW THE DIRECTIONS ON THE BLACKBOARD ON DISPOSAL OF CHEMICALS.

- ***Note that there are two different concentrations of the $\text{Fe}(\text{NO}_3)_3$!***
- As you begin to prepare the solutions, remember that you should not write on or put stickers on the cuvetts as this could interfere with the absorption readings.

Standard Curve

1. Obtain 5 clean and dry test tubes (**NOT** cuvetts) labeled 1-5 and fill each with exactly 2.50 mL of 0.200 M $\text{Fe}(\text{NO}_3)_3$ using a buret. Record the exact volume to the nearest 0.02 mL.
2. Again using a buret, add to test tube #1, exactly 0.50 mL of 0.00200 M KSCN solution, to test tube #2, 0.75 mL of 0.00200 M KSCN solution and so on in increments of 0.25 mL.
3. Finally, add enough 0.5 M HNO_3 to each of the test tubes so that the final volume in each tube totals 10.00 mL. (The volume of HNO_3 should have been calculated beforehand as part of the pre-lab assignment.) Mix thoroughly by covering with Parafilm and inverting the tubes numerous times until the contents are well mixed.
4. As usual, record the Instrument ID #. Examine the box of cuvetts assigned to you. Be sure they are clean and dry. If a cuvet is wet, rinse it a couple times with small quantities of the solution you are about to use. Pour the contents of each test tube into a cuvet, filling it about $\frac{3}{4}$ full. Set the spectrophotometer to 447 nm and zero the instrument with a cuvet filled with **0.5 M HNO_3** . Remember to wipe the sides of each cuvet with Kimwipes before placing it into the instrument. Record the absorbance starting from the most weakly absorbing and working towards the most intensely colored. *Do not cleanup until you have produced an acceptable Standard Curve (see below.)*

CALCULATIONS FOR THE STANDARD CURVE (to be completed before leaving)

Summarize the data needed to produce the standard curve by completing the tables on the Calculations & Results Page, remembering that the concentration of $\text{Fe}(\text{SCN})^{2+}$ is equal to the initial concentration of SCN^- . Prepare the graph using Excel. Include the data for the blank in your graph. There should be 6 points in your graph. Display the trendline and the R^2 on your graph and record them also on the Calculations & Results Page. Please review the Checklist in Experiment 1 (or Appendix 2) as to what else must be on your graph. Your data points should all lie close to the trendline. If not, you may

have to prepare fresh samples for one or more of your data points. Consult with your instructor. This is why the graph should be completed in class before you cleanup!

Equilibrium Data (You must use the same spectrophotometer as in the calibration.)

5. Obtain 5 clean and dry test tubes and fill each with 5.00 mL of 0.00200 M $\text{Fe}(\text{NO}_3)_3$ using a buret. If a test tube is wet, rinse it several times with small portions of the solution.
6. Add exactly 1.00, 2.00, 3.00, 4.00, and 5.00 mL of 0.00200 M KSCN, respectively, to test tubes labeled 1, 2, 3, 4, and 5.
7. Finally, add enough 0.5 M HNO_3 to each of the test tubes so that the final volume in each tube totals 10.00 mL. (Again, the volume of HNO_3 should have been calculated beforehand.) Mix thoroughly by covering with Parafilm and inverting the tubes.
8. Record the temperature of one of your samples in your lab notebook.
9. Repeat Step 4 and record the absorbance for each of the 5 samples.
10. Dispose of all chemicals in the designated waste container in the hood.

CALCULATIONS FOR THE EQUILIBRIUM DATA (Complete in class if time permits.)

Use the trendline equation from the standard curve to calculate the concentration of $\text{Fe}(\text{SCN})^{2+}$ in each tube and record on the Calculations and Results Page. Show your calculations on a separate sheet of paper.

Complete the ICE Table for each of the 5 samples and enter the equilibrium constant values on the Calculations & Results Page. (Reminder: Do not write “X” but put the actual values in.) Calculate an average for the equilibrium constant, and the error and percent error for your average.

Prepare your lab notebook by copying NEATLY, the Data Table from the next page into your notebook.

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Copy these Data Tables neatly in your lab notebook prior to arriving to class.

Spectrophotometer ID #: _____

STANDARD CURVE DATA

Table 8.1: Volume of reagents to be used

Tube #	Vol. of 0.200M $\text{Fe}(\text{NO}_3)_3$	Volume of 0.00200M KSCN	Volume of 0.500M HNO_3	Total Vol.
1	2.50 mL	0.50 mL	7.00 mL	10.00 mL
2	2.50 mL	0.75 mL	6.75 mL	10.00 mL
3	2.50 mL	1.00 mL	6.50 mL	10.00 mL
4	2.50 mL	1.25 mL	6.25 mL	10.00 mL
5	2.50 mL	1.50 mL	6.00 mL	10.00 mL

Table 8.2: Concentrations for Standard Curve

Tube #	Concentration of Fe^{3+}	Concentration of SCN^-	Conc. of $\text{Fe}(\text{SCN})^{2+}$	Absorbance
0	0.0000 M	0.0000 M	0.0000 M	0.000
1	0.0500 M	1.0×10^{-4} M	1.0×10^{-4} M	
2	0.0500 M	1.5×10^{-4} M	1.5×10^{-4} M	
3	0.0500 M	2.0×10^{-4} M	2.0×10^{-4} M	
4	0.0500 M	2.5×10^{-4} M	2.5×10^{-4} M	
5	0.0500 M	3.0×10^{-4} M	3.0×10^{-4} M	

EQUILIBRIUM DATA: *Temperature of one of the samples:* _____

Table 8.3: Volume of reagents to be used

Tube #	Vol. of 0.00200M $\text{Fe}(\text{NO}_3)_3$	Volume of 0.00200M KSCN	Volume of 0.500M HNO_3	Total Vol.
1	5.00 mL	1.00 mL	4.00 mL	10.00 mL
2	5.00 mL	2.00 mL	3.00 mL	10.00 mL
3	5.00 mL	3.00 mL	2.00 mL	10.00 mL
4	5.00 mL	4.00 mL	1.00 mL	10.00 mL
5	5.00 mL	5.00 mL	0.00 mL	10.00 mL

Table 8.4: Concentrations for Equilibrium Calculations

Tube #	Initial Concentration of Fe^{3+}	Initial Concentration of SCN^-	Absorbance	Equilibrium* Conc. of $\text{Fe}(\text{SCN})^{2+}$
1	0.00100 M	2.00×10^{-4} M		
2	0.00100 M	4.00×10^{-4} M		
3	0.00100 M	6.00×10^{-4} M		
4	0.00100 M	8.00×10^{-4} M		
5	0.00100 M	10.0×10^{-4} M		

Calculations & Results:

Sec: _____

Name: _____

Partner's Name : _____

STANDARD CURVE:*List in order from lowest concentration to highest.*

[Fe(SCN) ²⁺]	Absorbance
0.000 M	0.000

Trendline Equation =

 $R^2 =$ **EQUILIBRIUM RESULTS:**

Temperature of samples =

Tube #	Initial [Fe ³⁺]	Initial [SCN ⁻]	Absorbance	[Fe(SCN) ²⁺] at Equilibrium*
1				
2				
3				
4				
5				

*Calculated from the standard curve

*Show calculations for each test tube on a separate sheet of paper.***ICE Table Test tube # 1** *Reminder: Do not write "X" but use the actual numbers. See p.79.*

	[Fe ³⁺]	[SCN ⁻]	[Fe(SCN) ²⁺]
Initial			0.00 M
Change			
Equilibrium			

Cont'd.
next page

ICE Table Test tube # 2

	$[\text{Fe}^{3+}]$	$[\text{SCN}^-]$	$[\text{Fe}(\text{SCN})^{2+}]$
Initial			0.00 M
Change			
Equilibrium			

ICE Table Test tube # 3

	$[\text{Fe}^{3+}]$	$[\text{SCN}^-]$	$[\text{Fe}(\text{SCN})^{2+}]$
Initial			0.00 M
Change			
Equilibrium			

ICE Table Test tube # 4

	$[\text{Fe}^{3+}]$	$[\text{SCN}^-]$	$[\text{Fe}(\text{SCN})^{2+}]$
Initial			0.00 M
Change			
Equilibrium			

ICE Table Test tube # 5

	$[\text{Fe}^{3+}]$	$[\text{SCN}^-]$	$[\text{Fe}(\text{SCN})^{2+}]$
Initial			0.00 M
Change			
Equilibrium			

Equilibrium constant: *Show calc. setups on your own paper.*

K_{eq} #1	K_{eq} #2	K_{eq} #3	K_{eq} #4	K_{eq} #5	Average K_{eq}

The literature value for the equilibrium constant is 138 (Ref. 1). Calculate the error and percent error for your average equilibrium constant. Watch your sign! Show set up here.

Reference 1: Day & Underwood, "Quantitative Analysis" 1958 p.181