Experiment 7

THE IRON(III) – THIOCYANATE REACTION SYSTEM

Prepared by **Ross S. Nord**, Chemistry Department, Eastern Michigan University

PURPOSE

To investigate a novel reaction system by utilizing a spectrophotometer.

REACTING TO COMPLETION VS. REACHING EQUILIBRIUM

A typical assumption, initially made when studying chemistry, is that all reactants completely react to generate products. This picture is slightly complicated by the idea of the limiting reactant. In this case, one reactant is completely consumed and the other reactants are in excess (i.e., there will be some leftover).

Subsequently, the concept of equilibrium is introduced (the rate that reactants are converted to products is the same as the rate that products are back-reacting to yield reactants) and we learn that all reactions reach equilibrium. At the end of the reaction, both reactants and products still exist.

So, if all reactions reach equilibrium, why start by giving the impression that reactions go to completion? One reason is that it is much simpler to understand than equilibrium. Once the simpler picture is mastered, the more complicated idea of equilibrium is easier to grasp. A second reason is that a great many reactions effectively go to completion because the amount of reactant left at equilibrium is so small that it can safely be ignored.

HOW CAN WE TELL IF A REACTION GOES TO COMPLETION?

Typically, the easiest way to tell is to add more of each of the reactants (one at a time). If the reaction had gone to completion, adding more of a reactant present in excess will not result in the production of any additional product. Only adding the limiting reactant will increase the amount of product formed.

Conversely, if the reaction was at equilibrium, some of all of the reactants are still present. Thus, there will be additional product formed when more of any of the reactants is added (as predicted using Le Châtelier's principle).

IN THIS EXPERIMENT

Several mixtures of colorless Fe^{3+}(aq) and SCN^-(aq) will be prepared. Each will react to produce a colored product, $FeSCN^{2+}$(aq). So, the absorbance of the solution can be used to measure the amount of product generated. By varying the amounts of reactants used and observing the amount of product generated, it will be determined whether the reaction goes to completion or reaches equilibrium. Once this is determined, additional qualitative and quantitative studies will be conducted to further explore this reaction system.

PRE-LABORATORY PREPARATION

1. Read the background, procedure, and data analysis sections of the experiment.
2. Complete the PRELAB assignment in Canvas. Refer to your textbook and the various sections of the experiment as needed.

EXPERIMENTAL SECTION

REAGENTS PROVIDED

$Fe(NO_3)_3$(aq), 0.010 *M*. This is prepared using 0.10 *M* HNO_3 as the solvent, since the acid stops insoluble iron hydroxides from forming.
KSCN(aq), 0.010 *M*.
HCl(aq), 1.0 *M*.
KSCN(s) and KNO_3(s).

Hazardous Chemicals

0.010 *M* $Fe(NO_3)_3$(aq) and 0.010 *M* KSCN(aq) are both toxic and irritants. Wash thoroughly if you come into contact with either solution.

WASTE DISPOSAL

All solutions should be discarded into a waste container in the hood.

PROCEDURE

You will do this experiment with a partner.

SETUP THE SPECTROPHOTOMETER

1. Turn on the LabQuest2. Connect and calibrate a SpectroVis spectrometer using a distilled water blank.

Tap on **Sensors**, then **Calibrate,** and then **USB: Spectrometer** to get to the calibration screen.

2. Change the mode to Time-Based.

Tap on the ***Mode*** button and choose ***Time Based*** from the scroll box. Then tap ***OK***.

In this mode, the absorbance is displayed in the meter box. It is not necessary to tap the Start or Stop button at any point in this experiment.

3. Choose to monitor absorbance at 470 nm.

Tap on the red meter box (which shows the absorbance), select ***Change Wavelength***, and enter 470. LabQuest2 will select the closest available wavelength to 470 nm.

The complex ion formed during the reaction is red/orange, so it most readily absorbs blue light. We have the literature value for the molar absorptivity at 470 nm, so we will use it.

PREPARATION OF SOLUTIONS

4. Pour 60 mL of stock iron(III) nitrate into a clean, dry 100-mL beaker.

Record the actual concentration of the $Fe(NO_3)_3$ on your Data Sheet.

5. Pour 60 mL of stock potassium thiocyanate into a clean, dry 100-mL beaker.

Record the actual concentration of the KSCN on your Data Sheet.

6. Rinse out a 100-mL volumetric flask with distilled water.

It is not necessary to dry the flask since more water will be added later.

7. Pipet 5.00 mL of the $Fe(NO_3)_3$(aq) into the clean 100-mL volumetric flask.

Remember to rinse the pipet with the iron(III) nitrate solution first. Use a 250-mL beaker as a temporary waste beaker to hold the rinsings.

8. Pipet 5.00 mL of KSCN(aq) into the same volumetric flask.

9. Fill the volumetric flask to the line with distilled water, cap it, and then mix thoroughly (by inverting several times).

Label this as solution 1.

10. Rinse a cuvet once with distilled water and then three times with solution 1.

The rinsings can go into your waste beaker. In fact, it is best to hold the cuvet and volumetric flask over the waste beaker while pouring solution into the cuvet.

11. Fill the cuvet with the solution you just prepared, dry the outside with a Kimwipe, and then measure its absorbance at 470 nm.

To measure an absorbance, just insert the cuvet into the spectrometer and record the displayed reading from the meter box.

Record the absorbance on your data sheet to the nearest 0.001. Set the volumetric flask and cuvet aside for possible later use. Do not discard the solution yet.

Hint: if the absorbance is less than 0.100 then either the spectrometer needs to be recalibrated or the solution was not prepared properly. Redo it or get help as needed.

12. Repeat steps 6-11 for solutions 2-4 using the amounts of iron(III) nitrate and potassium thiocyanate found in Table 1.

Label each solution and do <u>not</u> discard any of the solutions, even after the absorbance has been measured.

Table 1. Solution compositions.

solution number	Volume of $Fe(NO_3)_3$ (mL)	Volume of KSCN (mL)
1	5.00	5.00
2	10.00	5.00
3	5.00	10.00
4	10.00	10.00

DETERMINATION OF REACTION TYPE

13. Answer Data Analysis question 1. If you decide that the reaction in solution 1 is at equilibrium, follow the steps below under EQUILIBRIUM. If you decide that the reaction has gone to completion, follow the steps below under COMPLETION.

EQUILIBRIUM
(Skip if your reaction went to completion)

14. Create an ice-water bath by filling a 50-mL beaker with ice and adding water until the liquid level is about halfway up the beaker.

15. Remeasure and record (in the data table under Equilibrium) the absorbance of the cuvet containing solution 1.

We will be remeasuring the absorbance of each solution immediately before modifying it, as sometimes the absorbance will drift with time.

16. Immerse the cuvet containing solution 1 into the ice-water bath for two minutes. Dry the outside using a Kimwipe, and then measure and record its absorbance.

17. Remeasure and record the absorbance of unmodified solution 2.

18. Add one BB-sized (2-3 mm diameter) crystal of KNO_3 to the volumetric flask containing solution 2. Cap and invert the flask several times to dissolve the crystal.

The exact size of the crystal is not critical. However, a smaller crystal will dissolve faster. Do not refill the flask or add any additional distilled water.

19. Rinse and fill a cuvet with the modified solution 2. Measure & record its absorbance.

20. Remeasure and record the absorbance of unmodified solution 3.

21. Add one BB-sized (2-3 mm diameter) crystal of KSCN to the volumetric flask containing solution 3. Cap and invert the flask several times to dissolve the crystal.

Again, the exact crystal size is not critical and do not refill the flask.

22. Rinse and fill a cuvet with the modified solution 3. Measure & record its absorbance.

If the SpectroVis's absorbance reading disappears, this means the absorbance is too large to be measured accurately. If this occurs, write an absorbance of 3.000 on your data sheet.

23. Remeasure and record the absorbance of the cuvet containing solution 4.

24. Add two drops of 1.0 M HCl to the <u>cuvet</u> containing solution 4. Put a cap on the cuvet and invert it several times to mix. Measure and record the absorbance of this solution.

Skip to the Clean-Up section below.

COMPLETION
(Skip if your reaction reached equilibrium)

25. Prepare solution 5 by pipetting 15.00 mL of each reactant into a 100-mL volumetric flask and filling it with distilled water.

26. Rinse and fill a cuvet with solution 5. Measure the absorbance of this solution and record it on your data sheet.

27. Prepare a hot water bath by adding 200 mL of hot tap water to a 400-mL beaker.

Run the hot water until it is as hot as it can get. This can take a couple of minutes. **Caution**: the water can get very hot so be careful not to burn yourself.

28. Immerse the volumetric flask containing solution 5 into the hot water bath and let it sit for 10 minutes. After 10 minutes fill a clean cuvet with the solution and measure its absorbance.

Typically, a reaction's rate is affected by temperature (as it will speed up at higher temperatures). This step is designed to test whether or not the yield is also affected.

CLEAN UP

29. Shutdown the LabQuest2.

Tap ***File****, then* ***Quit***, ***Discard*** the data, tap on the ***System*** folder, ***Shut Down*** and, finally, ***OK***.

30. Dump all of the waste solutions from the cuvets, volumetric flasks, and 250-mL beaker into a waste container in the hood.

31. Rinse all of your glassware with distilled water. Dry it and return it to the drawer(s).

RETURN EVERYTHING TO WHERE IT WAS AT THE START OF LAB. HAVE AN INSTRUCTOR CHECK YOUR STATION BEFORE LEAVING.

Wash your hands before leaving lab.

____________________ __________ ____________________

Name Station Used Instructor/Day/Time

____________________ ____________________

Partner Station Checked & Approved

DATA SHEET

Be sure to record all data with the proper number of significant figures (and units when needed).

Concentration of the stock $Fe(NO_3)_3$ solution: ________________________

Concentration of the stock KSCN solution: ________________________

Volumes Used and Absorbances for the Four Solutions Prepared:

	Volume of $Fe(NO_3)_3$ Used (mL)	Volume of KSCN Used (mL)	Absorbance
Solution 1	5.00	5.00	
Solution 2	10.00	5.00	
Solution 3	5.00	10.00	
Solution 4	10.00	10.00	

Equilibrium: (Skip this section if your reaction went to completion)

	Unmodified Absorbance	Cooled/Modified Absorbance
Solution 1		
Solution 2		
Solution 3		
Solution 4		

Completion: (Skip this section if your reaction reached equilibrium)

	Volume of $Fe(NO_3)_3$ Used (mL)	Volume of KSCN Used (mL)	Absorbance
Solution 5	15.00	15.00	
Solution 5 heated			

DATA ANALYSIS

All calculations should be clearly organized, make proper use of significant figures, and include the units.

1. Decide whether the reaction in solution 1 goes to completion or reaches equilibrium.
(a) Compare the absorbances for solutions 1 & 2. Did the amount of product produced significantly increase (by more than 25%) when the concentration of $Fe(NO_3)_3$ is doubled? (Recall that the absorbance is proportional to the concentration of product.)

(b) Compare the absorbances for solutions 1 & 3. Did the amount of product produced significantly increase (by more than 25%) when the concentration of KSCN is doubled?

(c) Based upon your answers to questions (a) and (b), decide if the reaction has a limiting reactant. If so, the reaction has gone to completion, if not, the reaction has reached equilibrium. Circle the appropriate choice below: [Review the background material on the first page of the experiment and then chat with the instructor, if necessary, if you are uncertain.]

The reaction went to completion   The reaction reached equilibrium

2. Theoretically, if a reaction goes to completion and one reactant is in large excess, is it possible for the answers to questions 1(a) and 1(b) to both be no? If so, explain how.

EQUILIBRIUM (Skip this section if your reaction went to completion)

3. Circle your choices from the pairs provided in the following statement:
Submerging solution 1 in an ice bath caused the absorbance to (***increase***, ***decrease***) meaning that the concentration of product (***increased***, ***decreased***). This implies that the equilibrium shifted to favor the (***reactants***, ***products***) meaning that heat is a (***reactant***, ***product***) in this reaction. Therefore, this reaction is (***endothermic***, ***exothermic***).

As the temperature increases, the value of K_c for this reaction will (***increase***, ***stay the same***, ***decrease***).

4. Calculate K_c for the reaction, using the solution 1 room-temperature data, following steps (a-e):
(a) Calculate the concentration of product formed in solution 1 using Beer's Law ($A=\varepsilon bc$, b=1.00 cm), its measured absorbance (at room temperature), and a molar absorptivity of 4.80×10^3 cm^{-1} M^{-1}. Use the Solution 1 Unmodified Absorbance (the second time you measured it, but still at room temperature).

(b) Use the concentration of the stock $Fe(NO_3)_3$ provided, and the volume used, to perform a dilution calculation and determine the initial concentration of Fe^{3+} in the 100-mL volumetric flask.

(c) Calculate the initial concentration of SCN^- in solution 1 by repeating step (b) for KSCN.

(d) In the table below, insert your answers for parts (b) and (c) for the initial concentrations of reactants and insert your answer to part (a) for the equilibrium concentration of product. Complete the table.

Net ionic reaction: $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$

Initial (M)	(b)	(c)	0
Change (M)			
Equilibrium (M)			(a)

(e) Use the equilibrium concentrations of the three species to calculate K_c for the reaction.

5. Solid potassium nitrate was added to solution 2.

(a) Write the formulas (including charges) of the ions formed when KNO_3 dissolves.

(b) When the KNO_3 was added to solution 2, did the absorbance change significantly (more than 25%)?

(c) If so, briefly explain which ion is affecting the equilibrium and how. If not, give the general name assigned to ions that are present in a solution but not participating in a reaction.

6. Solid potassium thiocyanate was added to solution 3.

(a) Write the formulas (including charges) of the ions formed when KSCN dissolves.

(b) When the KSCN was added to solution 3, did the absorbance change significantly (more than 25%)?

(c) If so, briefly explain which ion is affecting the equilibrium and how. If not, give the general name assigned to ions that are present in a solution but not participating in a reaction.

7. Adding HCl, to solution 4, affects the equilibrium because $FeCl_4^-$ is a stable complex ion that can form from Fe^{3+} and Cl^- in aqueous solution.

(a) Should the $[Fe^{3+}]$ in the cuvet initially increase or decrease when the HCl is added?

(b) As the $[Fe^{3+}]$ changes as predicted in part (a), what effect should this have on the $[FeSCN^{2+}]$? (Refer to the reaction given in question 4(d) and consider Le Châtelier's principle.)

(c) As the $[FeSCN^{2+}]$ changes as predicted in part (b), what effect should this have on the absorbance?

(d) Did your experimental absorbance change as predicted in part (c)? If not, resolve the discrepancy.

COMPLETION (Skip this section if your reaction reached equilibrium)

8. Based upon the absorbances of solutions 1, 2, & 3, which of the two reactants is the limiting reactant? Fully explain how you decided which one is limiting.

9. If the limiting reactant is $Fe(NO_3)_3$ the reaction should have gone to completion in solution 3. If the limiting reactant is KSCN the reaction should have gone to completion in solution 2. The amount of limiting reactant, and the absorbance, can be used to calculate the molar absorptivity of the product.

(a) For the solution where the reaction went to completion, what volume of limiting reactant was used?

(b) Use the concentration of the stock limiting reactant solution provided to perform a dilution calculation and determine the concentration of limiting reactant in the 100-mL volumetric flask.

(c) Assuming that one mole of the product forms for each mole of limiting reactant used, the answer to part (b) is also the concentration of the product that formed. Use this concentration, the measured absorbance, and Beer's Law ($A=\varepsilon bc$, $b=1.00$ cm) to determine the molar absorptivity of the product.

10. In solution 5, the concentration of the limiting reactant was approximately tripled and so the concentration of product obtained should be tripled as well.

(a) Using the molar absorptivity just determined, and the absorbance of solution 5, calculate the concentration of product obtained in solution 5.

(b) From the volume of limiting reactant used, calculate the expected concentration of product in solution 5 (following the same procedure as in questions 9(a) and (b), above).

(c) Calculate the % yield by dividing the actual concentration obtained in step (a) by the expected concentration calculated in step (b) and multiply by 100%.

(d) If your percent yield is less than 90% or greater than 110%, explain what might cause this deviation.

11. The effect of temperature on the yield of product.

(a) Based upon the absorbance of solution 5 after it had sat in the hot water bath, does the yield of product increase or decrease with temperature?

(b) Calculate the % yield at the higher temperature.