

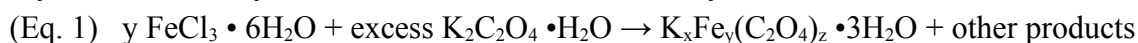
Experiment 1: Synthesis and Analysis of an Inorganic Compound

CH3500: Instrumental Analysis, Plymouth State University

Adapted from Johnson, R.C. "Convenient procedure for the preparation of potassium trioxalatoferate(III)," *Journal of Chemical Education* **47**, 702 (1970); Olmsted, J. "Preparation and analysis of potassium tris(oxalato)ferrate(III)trihydrate: A general chemistry experiment," *Journal of Chemical Education* **61**, 1098 (1984); "Preparation of a Complex Iron Salt" and "Analysis of a Complex Iron Salt," available at <https://eee.uci.edu/programs/gchem/1LC.htm>; "Synthesis of a Coordination Compound Containing Iron and Analysis of this Compound Using Redox Methods" available at <http://people.sps.lane.edu/bgreen/labsynfes034.pdf>; and "The Synthesis of a Complex Iron Salt," available at <http://pages.cms.k12.nc.us/ulvs1-d/gems/kurt Niedenzu/GreenCrystalLabword.doc>.

Introduction: This lab will be done over the course of two lab periods. In the first, you will synthesize the compound, and in the second you will analyze it to determine its molecular formula.

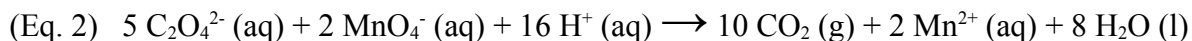
As you will learn about in detail this semester, inorganic compounds may contain a variety of species, including ions, ligands, metal centers, and independent molecules. In this lab, you will synthesis a complex iron salt with the formula $K_xFe_y(C_2O_4)_z \cdot 3H_2O$, where $C_2O_4^{2-}$ is the oxalate ligand. The "dot" before H_2O indicate these are "waters of hydration", which means the three water molecules are loosely bound in the crystal. The overall reaction for the synthesis is:



In inorganic synthesis, the desired product is frequently formed and isolated by crystallization from a reaction mixture. Because the reaction mixture may contain excess reactants and other products, the crystals are likely to be relatively impure. The crystals can be separated from the impure solution (often called the "mother liquor") by filtration or decantation and then washed. However, washing will not remove impurities occluded within the crystals. A standard method for purifying the product is recrystallization. The product is redissolved in a minimal amount of an appropriate solvent, generally while heating. Slow cooling of the solution results in slow crystal growth, producing pure crystalline product.

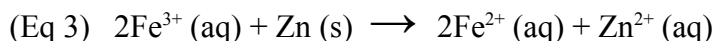
An important factor in syntheses is the actual quantity of desired product obtained compared to the theoretical amount predicted on the basis of the stoichiometry of the reaction. The ratio of the mass of the actual product to the theoretical amount is the 'percent yield'. There are many reasons why the actual yields are not 100%: the reaction may reach equilibrium before going to completion, the reactants may undergo reactions other than the one leading to the desired product, the desired product may undergo further reactions, product may be lost in the isolation steps, the product may be contaminated, etc.

The oxalate ion ($C_2O_4^{2-}$) in the compound will be analyzed by titration with potassium permanganate ($KMnO_4$) according to the reaction:

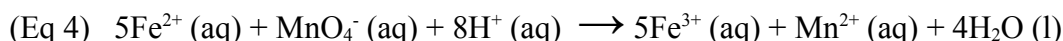


Before you can perform the titration, you will need to standardize the potassium permanganate using sodium oxalate ($Na_2C_2O_4$), according to the same reaction.

The amount of iron in the complex will be analyzed through three reactions. First, the oxalate ion is destroyed by reaction with permanganate, according to the reaction above. Second, the ferric iron is reduced to ferrous iron by reaction with zinc:



Finally, the ferrous iron is titrated with permanganate:



Safety Considerations:

- Permanganate (MnO_4^-) is toxic and an environmental pollutant. All solutions containing permanganate, including the initial washes of glassware, should be disposed of in labeled waste containers. Care should be taken to avoid contact with permanganate solutions. Wash your hands and clean up immediately if any solution is spilled.
- Strong acids are used and heated in this lab.
- In some steps, water will be added to a strong acid. This is the opposite order from what is normally recommended! Be careful, go slowly, and stir constantly.

Procedure

- You will work with a partner for both parts of this lab
- Remember to record what you do, data collected, and observations at each step in the procedure.

WEEK 1

A. Preparation of $\text{K}_x\text{Fe}_y(\text{C}_2\text{O}_4)_z \cdot 3\text{H}_2\text{O}$

1. In a 100 mL beaker, weigh out approximately 5 g of potassium oxalate monohydrate, ($\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$). Record the exact mass using all the digits available on the balance.
2. Using a graduated cylinder, add 10 mL of distilled water to the beaker. Gently add a small magnetic stir bar. Heat and stir this solution gently (do NOT let it boil!) on a hotplate until all of the potassium oxalate has dissolved.
3. While the potassium oxalate solution is heating, you can make your solution of iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$). In a second 100 mL beaker, weigh out approximately 2.5 g of iron(III) chloride hexahydrate. Record the exact mass using all the digits available on the balance.
4. Add 5 mL of DI water to the iron(III) chloride hexahydrate. Heat this solution gently on a hotplate (do NOT let it boil!) and swirl to dissolve the solid. If large amounts of the solid do not dissolve, add a few squirts of DI water and continue heating and swirling. Do NOT add more than about 3 mL of water.
5. Set up a small glass funnel with a piece of filter paper. Filter the iron(III) chloride hexahydrate solution from Step 4 into the hot potassium oxalate solution. Rinse filter paper once with less than 1 mL of water (few squirts from a squirt bottle).
6. Use a magnet to remove the stir bar. Cool the solution for 20 - 40 minutes by placing the beaker in ice (take care that it does not sink into the ice water!). Crystals should form during this time.
7. After giving the crystals ample time to form, carefully decant and discard the solvent.
8. Add 8 ml distilled water to the crystals. Heat gently with swirling to completely dissolve the crystals. If crystals remain undissolved, add a few squirts of DI water and continue heating and swirling. Do NOT add more than about 3 mL of water. If some dark residue remains undissolved, carefully decant the clear solution into another beaker and discard the residue.
9. Cover the beaker with a watch glass and set it in your drawer until the next lab period in order to allow the crystals to form.
10. Clean a small sample bottle. Allow it to drain & thoroughly dry it with a paper towel.
11. Clean your glass ware, properly dispose of all waste, and wipe down your lab bench.

12. Answer the Analysis Questions (below) for Week 1 in your lab notebook. Sign and date the last page of your experiment. Ask the Instructor to check and sign your lab notebook. Remove your duplicate pages, staple them together, and hand them in.

WEEK 2

- This lab involves several steps, some of which may be done concurrently. It is advisable to divide up the tasks between lab partners and work in parallel.

B. Isolation of $K_xFe_y(C_2O_4)_z \cdot 3H_2O$

1. Place the beaker with crystals in ice while you do Step 2.
2. Set up a vacuum filtration apparatus with a Büchner funnel. Turn on the vacuum and squirt the paper with a small amount of 50% ethanol/water to seat the filter paper.
3. Filter the crystals. Leave the vacuum on until Step 8
4. Use a minimal amount of 50% ethanol/water to transfer any remaining crystals from the beaker and to wash the crystals on the filter paper (approximately two 3-mL portions).
5. If the crystals are clumped together on the paper, use a glass stirring rod to spread them evenly over the filter paper and break up any clumps.
6. Rinse the stirring rod onto the filter paper, and rinse the crystals with a small amount of chilled acetone (approximately two 3-mL portions).
7. Leave the vacuum pump on to dry the crystals for 10 min.
8. Record the exact mass of your cleaned sample bottle, using all the digits on the balance.
9. Turn off the vacuum pump. Carefully remove the filter paper containing the crystals and transfer them into the sample bottle. Record the exact mass of the sample bottle and crystals, using all the digits on the balance. Label the bottle with your name and the contents ($K_xFe_y(C_2O_4)_z \cdot 3H_2O$). (*Note: the crystals are light-sensitive. Store in a capped, amber or aluminum foil-covered bottle in a dark place when not using them.*)

C. Standardization of $KMnO_4$.

- *At least three titrations must be done; it is recommended that the first be done quickly as a "throw away".*
 - *It is useful and recommended that you set up a table of Mass of Sodium Oxalate, Initial Volume, Final Volume, Volume Added, and Corrected Volume Added for the titrations.*
 - *Properly dispose of all solutions containing $KMnO_4$.*
1. Clean a buret and rinse it with a small amount of the $KMnO_4$ solution.
 2. Fill a buret with the $KMnO_4$ solution. *Note: the solution is very dark purple, so read the volumes from the top edge of the liquid instead of the bottom of the meniscus.*
 3. Using weigh paper, weigh out 0.12 g of sodium oxalate ($Na_2C_2O_4$). Record the exact mass using all the digits on the balance.
 4. Transfer the sodium oxalate to a 250 mL Erlenmeyer flask and dissolve in 10mL of 6M H_2SO_4 . CAREFULLY and SLOWLY add 65 mL of DI water.
 5. Heat the solution of sodium oxalate in the Erlenmeyer flask to 80-90 °C. TAKE CARE when heating this strong acid solution! Do NOT let it boil! *Note: When you remove the thermometer, be sure to rinse it into the flask so you will not lose sodium oxalate.*

- Record the initial reading on the buret to the nearest 0.01 mL and begin titrating. Add KMnO_4 in small portions and swirl the solution. The purple solution will lose its color as it falls into the hot solution, but if KMnO_4 is added too rapidly, a brown color due to the formation of manganese dioxide (MnO_2) will appear. Excess oxalate will reduce the MnO_2 momentarily, but try to titrate slowly enough to not produce the brown color to avoid overshooting the endpoint.
- As you near the endpoint, you should be adding one drop at a time. At the endpoint, a faint color will persist in the solution. Record the final volume. If you are near the endpoint and think you may overshoot it, record the volume and then add one drop. This way, if you do overshoot, you have the final volume recorded and will not have to perform an additional trial of the titration.
- Repeat this procedure (Steps 3-7) at least two more times. You may need to do one or two more until you have at least two runs that you consider "good" and that agree with one another reasonably well. *Note: you do NOT need to refill the buret between titrations if there is more than enough remaining for the next titration.*
- Run a blank for this titration in the following way (to account for possible impurities in the sulphuric acid solution that may react with the potassium permanganate and bring error to your data): Add 65 mL of DI water and 10 mL 6M H_2SO_4 to a clean Erlenmeyer flask and heat it to 80-90 °C. Titrate this with the KMnO_4 solution (this may only take one or two drops).
- Calculate the corrected volumes of KMnO_4 needed for each titration by subtracting the Blank volume found in Step 9 from each titration volume.

D. Determination of Oxalate Stoichiometry

This procedure is essentially the same titration as in Part C, except the iron salt is used instead of sodium oxalate. See "Notes" from Part C. A similar table to collect data is appropriate here.

- Refill the buret with the KMnO_4 solution.
- Using weigh paper, weigh out 0.12 g of your iron complex. Record the exact mass using all the digits on the balance.
- Transfer the iron complex to a 250 mL Erlenmeyer flask and dissolve in 10mL of 6M H_2SO_4 . CAREFULLY and SLOWLY add 65 mL of DI water.
- Using a disposable pipette, add 1 mL of conc. H_3PO_4 . (*Note: ferric iron has a yellow color in water. The phosphate binds the iron to make a colorless compound.*)
- Heat the solution in the Erlenmeyer flask to 80-90 °C. TAKE CARE when heating this strong acid solution! Do NOT let it boil! *Note: When you remove the thermometer, be sure to rinse it into the flask so you will not lose any analyte.*
- Titrate the solution to the endpoint. (See notes in Part C, Steps 6-7)
- Repeat this procedure (Steps 2-6) at least two more times. *Note: you do NOT need to refill the buret between titrations if there is more than enough remaining for the next titration.*
- Calculate the corrected volumes of KMnO_4 needed to titrate the solutions by subtracting the Blank Volume found in Part C, Step 9.

E. Determination of Iron Stoichiometry

- Weigh out 2g of your iron complex in a 250 mL beaker.
- Add 100 mL of distilled water and 30 mL of 6M H_2SO_4 . Add a stir bar. Heat and stir this solution carefully until the compound is dissolved.
- To destroy the oxalate ions, heat the solution to near boiling and add 3% KMnO_4 (NOT YOUR

- STANDARDIZED SOLUTION) with disposable pipette until the solution remains purple or brown. This may require several milliliters, but there is no need to be careful about measuring.
- Heat this solution to near boiling, take the beaker off the heat and place it on an un-heated stir plate under the hood. *Perform Step 5 while waiting for solution to heat.*
 - Prepare a vacuum filtration setup with a clean receiving vacuum flask.
 - CAREFULLY add 10g of zinc powder and stir to avoid splashing. The solution will turn from brown to yellow to colorless. You want all of the yellow color to disappear but you do not want to add a large excess of zinc. If the solution turns clear before you have added all the zinc, stop adding zinc. If you have added all the zinc and the yellow color persists, cover the solution and stir for a few minutes. If the color does not disappear, add 0.5 g of zinc.
 - Quickly filter the excess zinc because iron(II) tends to oxidize to iron(III) in the presence of air. Rinse the beaker and the filter cake with three 10 mL portions of DI water.
 - Quantitatively transfer the filtrate to a 250 mL volumetric flask. (Use a glass funnel. Rinse the vacuum flask three times with distilled water, adding the rinses to the volumetric flask). Dilute the solution with distilled water, but NOT all the way to the mark. Swirl the solution to mix thoroughly as you add the water.
 - If the solution in the flask is hot to the touch, put the flask on ice for a few minutes until you can handle it comfortably.
 - Add DI water to the mark, cap the flask, and invert to mix.
 - Fill a buret with the standardize KMnO_4 (Part C). Record the initial volume.
 - Use a volumetric pipette to transfer 50 mL of the solution into an Erlenmeyer flask.
 - Reheat the Erlenmeyer flask to near boiling.
 - Begin titrating as soon as the solution is near boiling. Start the titration by adding KMnO_4 at a fast drip, swirling constantly. You do not want the solution to become cloudy. Slow down the addition of KMnO_4 , but keep swirling at all times, when you are approaching the endpoint. The endpoint is determined by a color change from clear yellow to a clear peach. The color should persist for 20-30 seconds.
 - Perform two more titrations, repeating Steps 12-14. You may wish to do the first titration very quickly as a "throw away."

Answer the Analysis Questions (below) for Week 2 in your lab notebook. Sign and date the last page of your experiment. Ask the Instructor to check and sign your lab notebook. Remove your duplicate pages, staple them together, and hand them in.

Analysis

Week 1

- Using the actual masses of the reagents you used, calculate the moles of potassium oxalate monohydrate and iron (III) chloride hexahydrate you reacted together.
- Explain two things in the procedure that may reduce the final percent yield.
- In Step 6, initial crystals were grown rapidly by cooling the solution with ice. In Step 9 you set up a slow recrystallization, which will occur over the next week. Why should the recrystallization be done slowly?

Week 2

1. Calculate the concentration of the KMnO_4 solution using your data from Part C. Use the proper number of significant figures based on the digits available from the buret and the balance. You may leave out the result from the first titration if you used it as a "throw away."
2. From your calculated value of the KMnO_4 concentration, calculate the moles and mass of oxalate present in each sample of your iron complex you titrated in Part D (it is recommended that you use a table to collect these numbers). *Notice the 5:2 ratio from Equation 3 in the Introduction.*
3. From your calculated value of the KMnO_4 concentration, calculate the moles of Fe in each of the 50 mL aliquots you titrated in Part E. *Notice the 5:1 ratio from Equation 5 in the Introduction.*

Lab Report

Your lab report is due by lecture on Wednesday, Sept 15. Your report must be handed in BOTH electronically and in hard copy form. See the document "InorgChem-LabReportGuide.pdf" on the course website (http://oz.plymouth.edu/~jsduncan/courses/2010_Fall/InorganicChemistry) for guidelines on writing your report.

A re-write of your lab report, addressing grader's comments, is due by lecture, Friday, Sept 24 in both electronic and hard copy form.

Questions to be answered in the lab report:

1. What is the correct stoichiometry of your product, $\text{K}_x\text{Fe}_y(\text{C}_2\text{O}_4)_z \cdot 3\text{H}_2\text{O}$? What are the values of X, Y, and Z?
2. What was your percent yield?